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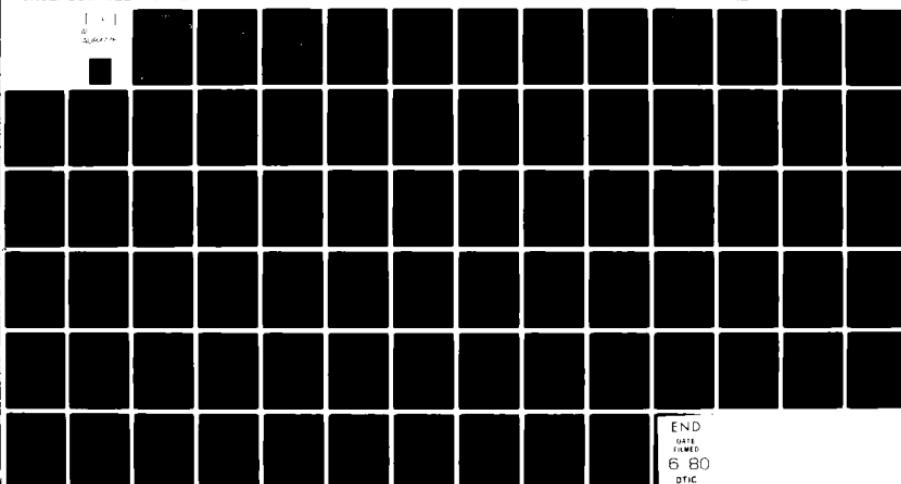
LOW TEMPERATURE FLUORINATION OF AEROSOL AND CONDENSED PHASE SOL--ETC(U)

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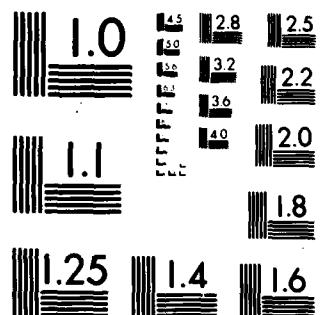
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TECHNICAL REPORT No. 2

Low Temperature Fluorination of Aerosol and
Condensed Phase Sol Suspensions of Hydrocarbons
Utilizing Elemental Fluorine

by

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mass transport which results in long reaction times and the essentially batch nature of gradient reactor process.

This report outlines in chronological fashion the systematic advances in development of Aerosol Fluorination technology. We have developed a four stage aerosol fluorination reactor which can be described as a dynamic concentration-gradient, temperature gradient reactor which achieves optimum control of the reaction between elemental fluorine and several hydrocarbon systems. Furthermore the system has shown the ability to effectively control the degree of hydrogen substitution at any level of fluorination up to and including perfluorination.

A detailed study of the effect of reaction parameters on the efficacy and efficiency of fluorination has been undertaken for neopentane. The data presented show both the controllability and the variability of the reactor system. A detailed study of product distributions and isomer distributions suggest that preferential reaction occurs for certain types of hydrogens and that isomer distributions are not determined solely by statistical probability.

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Introduction

This report outlines the further development of an aerosol fluorinator, a new concept in low temperature direct fluorination. The process involves the reaction of gaseous elemental fluorine upon a solid-phase, particulate aerosol at temperatures below room temperature. The rationale for the development of this method is that it is a flow process and has extensive flexibility which allows the optimum conditions of flow, temperature, fluorine concentration and reaction rate to be achieved without undue limitations arising from the physical state or volatility of the starting material. Practically any material which may be converted into a solid-phase particulate aerosol may be fluorinated by this method. Another advantage is that the degree of fluorine substitution is easily controlled by simply varying the fluorine concentration gradient and the molar ratios of hydrocarbon to fluorine. This is of major importance in further studies designed to achieve selectivity in fluorine attack at low temperatures. Technical Report No. 3 which is now in manuscript will outline a detailed study of the neopentane system which strongly suggests preferential attack on certain hydrogen environments within the neopentane system during fluorination giving nonstatistical isomer distributions.

The aerosol process represents the first major advance in direct fluorination since the developments of the "LaMar" technique by Lagow and Margrave^{1,2,3} and the "low-temperature, gradient (LTG) fluorination" techniques by Adcock, Marashin and Lagow.^{4,5,6,7,8} This process preserves the salient features of the gradient fluorination technique leading to high yields but overcomes two major drawbacks to the gradient process: (a) its batch nature and (b) its reliance on low temperature mass transport to insure maximum surface exposure to elemental fluorine. The need for mass transport at low temperatures unnecessarily slows the fluorination reaction leading to long reaction times.

This report describes in chronological fashion the development of the aerosol fluorination system since Technical Report No. 1. In part two of this report we describe the multistaging experiments which have led to the most versatile continuous operation, direct fluorination system in existence. This system can be described as a dynamic fluorine concentration gradient, temperature gradient aerosol reactor. This system has unprecedented control over the potentially violent direct fluorination reaction. Even at fluorine flows of 0.48 moles/hr F_2 , the system operates smoothly and without violence. We are currently constructing a larger version of the aerosol system for general preparative work because of the time and throughput advantages of the system over prior art. The only current limitation of the system is the relative low concentration of fluorine in the final stages (27 mole percent) which we are currently seeking solutions by utilization of diffusion technology and photochemical activation.

Description of the Process

The significant successes of the LTG direct fluorination technique and the intrinsic simplicity of direct fluorination led to a firm belief that a successful, general fluorination technique could be developed employing elemental fluorine. A critical analysis of the LTG reaction system produced a set of five conditions which we believe contribute to a high yield reaction. The conditions which we considered important are:

- (a) Fluorination of Molecules in the crystalline state.
- (b) A very high surface area exposed to gaseous fluorine.
- (c) Low temperature.
- (d) High initial dilution of fluorine gas.
- (e) A highly efficient mechanism of heat dissipation.

The crystalline matrix reduces hydrocarbon radical recombinations when radicals are formed under "dilute" conditions. The crystalline matrix acts as an energy sink to dissipate reaction energies. A high surface area promotes uniform attack by fluorine on all molecules. Low temperature reduces the vigor of reaction by an overall reduction in kinetic energy and by limiting the number of radical chain initiations. High initial dilution of fluorine reduces the overall reaction rate and reduces the likelihood of simultaneous attack by two fluorine molecules or radicals on adjacent sites on a molecule which would increase the degree of fragmentation. Effective heat dissipation would prevent the formation of "hot spots" and prevent combustion from occurring.

These conditions, however, must be modified if one is to achieve high degrees of fluorination over a reasonable time span. The concentration of fluorine must be increased to maintain a good reaction rate as the reactant molecules become more highly fluorinated and a greater percentage of collisions are ineffective. It is also beneficial in this regard to increase

the temperature. Since these conditions directly conflict with the desired initial conditions their imposition must be separated in time or in space. The LTG system simply changes the applied temperature gradient and increases the fluorine concentration over time.

Separation of the perfluorination enhancing conditions from the initial conditions in space requires that the reactant be mobile. This mobile species may then be induced to pass through progressively warmer regions which have higher degrees of fluorine concentration. A gaseous reactant would be mobile, of course, but the desirability of limiting collisions between hydrocarbon radicals and thus limiting coupling reactions giving tars and oils dictates a condensed, preferably crystalline, phase. A liquid reagent stream does not allow for the uniform, rapid mixing of the very reactive gaseous elemental fluorine thus preventing uniform, controlled attack and substitution of fluorine at every C-H bond.

In order to achieve gas-like mobility and retain crystallinity it is necessary to produce extremely small, solid particulates. These particulates may then be suspended and transported using a carrier gas. These particulates possess extremely high surface area which permits uniform attack by gaseous elemental fluorine on the suspended reactant. Extremely effective heat dissipation may be achieved by using helium as the carrier. Multiple collisions of the reactant particulates with the helium carrier gas molecules dissipate heat rapidly. Excess energy is continuously carried by the helium atoms to the walls of the reactor.

Principles of aerosol production are well developed. Our initial design ideas were developed from study of existing technology for producing aerosols which were developed primarily as an adjunct of atmospheric and industrial hygiene studies. Descriptive passages by N. A. Fuchs and A. G. Sutugin,⁹ R. D. Cadle¹⁰ and F. C. Goodrich¹¹ describe the requirements of generators

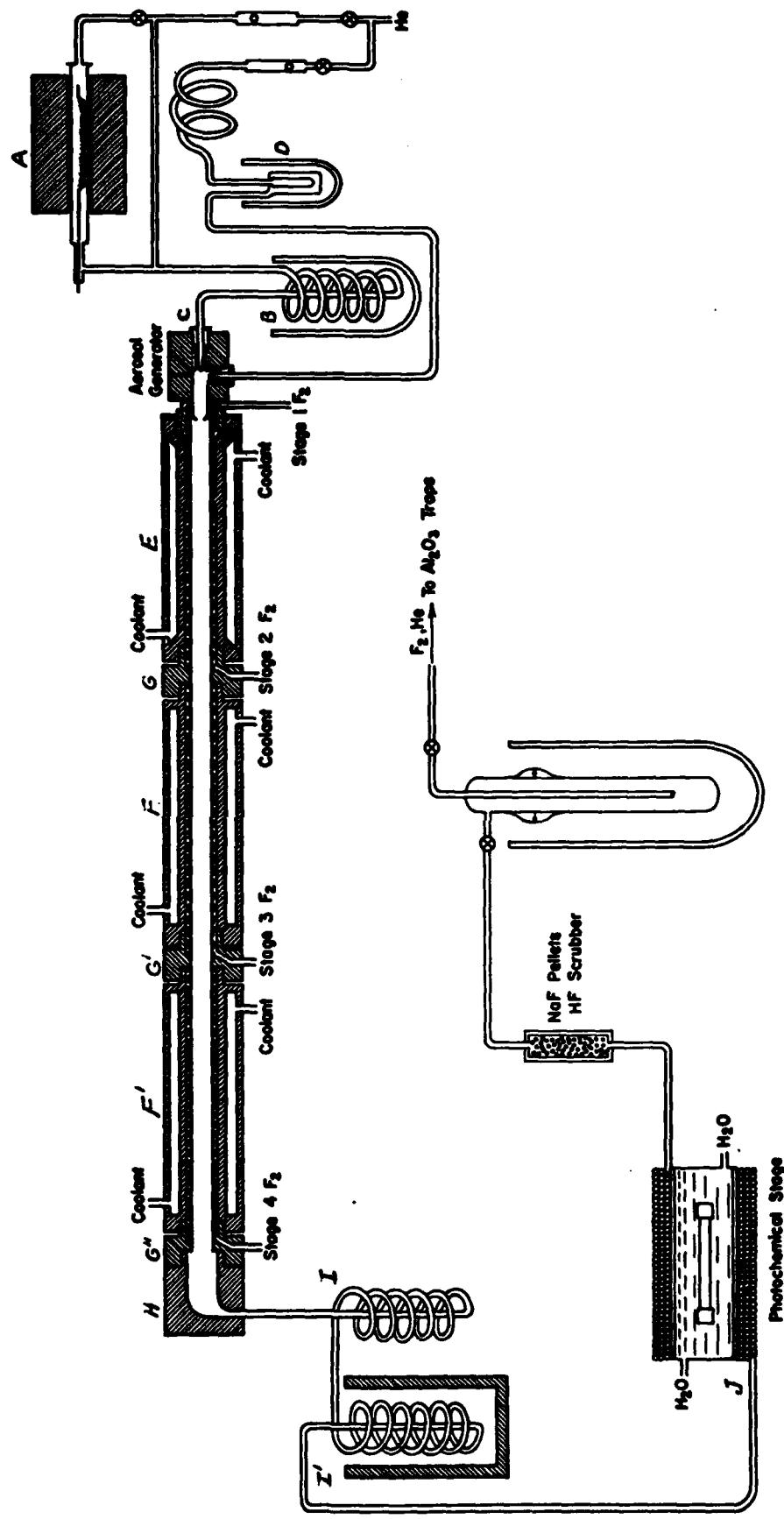
capable of producing aerosols. A more recent paper by A. G. Sutugin describes a mixer type generator which is generally applicable to the problem of steady state aerosol production in a flow reactor.¹² The major difference between our own independently developed design and that described by Sutugin is the subambient temperature capability of our design.

The aerosol fluorination system designed to produce a controlled, continuous stream of aerosol particulates includes the following components (Figure 1). A bed of sodium fluoride heated to 850°C (A) sublimes highly dispersed NaF particles (average radius; 17.5 Å.¹³) into the helium carrier gas. These particles serve as condensation nuclei for the hydrocarbon condensation. The carrier gas is chilled to near -196°C by passing through a liquid nitrogen cooled heat exchanger (B). The chilled carrier gas, helium in this embodiment, is mixed with a second gas stream containing the hydrocarbon vapor in a precise arrangement within the body of the generator (C). The hydrocarbon vapor in the stream produced by an evaporator device (D) will condense into aggregates around the sodium fluoride particles within the chilled carrier. The chilled aerosol is directly channeled into the reactor (E) where it is mixed with elemental fluorine in such a way as to produce uniform contact between the aerosol particles and elemental fluorine. The temperature of the reactor (E) is controlled by means of an integral heat exchanger which can provide variable temperatures from the cryogenic to the ambient range.

The aerosol generator system is of the evaporation-condensation type. It, however, seems likely that aerosol particulates generated by any mechanism; physical, chemical or mechanical; would work equally well. It is the high surface area created by extensive subdivision of aggregates that is essential to the process.

Having created a mobile reactant it is possible to separate in space the

FIGURE 1
AEROSOL FLUORINATOR



conditions giving low fragmentation, i.e., high initial dilution of fluorine, low temperature; from those conditions leading to high degrees of fluorination; i.e., increased fluorine concentration and temperature.

Modular design of the system has allowed for the addition of staging components following the reactor (E). Each staging component consists of a module (F) and a "staging insert." (G) A series of modules (F) connected to the reactor thus provide for independently controlled temperature zones, and the addition of "staging inserts," (G') allow the independently controlled injection of additional elemental fluorine. Using these devices hydrocarbon or other molecules may be controllably fluorinated to any degree including perfluorination. It is also conceivable that other reagents besides elemental fluorine can be introduced in the later stages to achieve functionalization, etc.

The addition of modules and staging inserts may be continued indefinitely by insertion ahead of the end cap (H). Each stage may be modified to provide for recycling of any or all of the various reacting species. In the system shown (Figure 1) a total of three staging inserts have been assembled giving in effect a four-stage aerosol fluorination reactor in which fluorine can be added in four independently controlled zones at three independently controlled temperatures.

In molecules which are exceptionally difficult to perfluorinate a heated coil I' and/or a flow type photochemical reaction stage (J) following stage 4 (Figure 1) have been developed which significantly activate the elemental fluorine or other reagent present in the reaction stream.

The multistaged aerosol fluorination reactor achieves optimum control over the potentially violent direct fluorination reaction. It is possible to expose the unfluorinated reactant to a very dilute, even distribution of elemental fluorine at low temperatures. Furthermore the condensed phase of

the aerosol particle distributes reaction heat evenly over a large number of molecules held in an ideally crystalline aggregate which may readily dissipate energy by multiple rapid collisions with helium gas. All of these effects serve to reduce the violence and heat accumulation which are primary concerns in direct fluorination. As the reactant molecule becomes more highly fluorinated and hence less vulnerable the aerosol aggregate is carried into regions of higher fluorine concentration, higher temperature and generally more rigorous conditions which tend to bring about higher degrees of fluorination.

This combination of conditions is unique to the aerosol fluorination reactor and provides in effect a dynamic, variable-fluorine-concentration-gradient, variable-temperature-gradient reactor.

Experimental PartGeneral

The three hydrocarbons investigated in these initial aerosol fluorination reactions are cyclohexane, a cyclic aliphatic hydrocarbon; 1,4-dioxane, a cyclic ether, and neopentane, a highly branched alkane. Selected physical properties for these compounds are listed in Table 1. Figure 2 shows the vapor pressure curves for cyclohexane and 1,4-dioxane from melting point to boiling point. Figure 3 shows the portion of these curves around room temperature (20° to 35°C) in more detail. Figure 4 gives the vapor pressure curve for solid and liquid neopentane from -78°C to its boiling point at $+9.5^{\circ}\text{C}$. Tables 2, 3 and 4 list the mass throughput of cyclohexane 1,4-dioxane and neopentane respectively versus flow-rate of the hydrocarbon carrier. Throughputs at room temperature were run with the carrier gas bubbling through the liquid hydrocarbon in a 250 ml r.b. flask fitted with dispersion tube. Throughputs at 0°C or below (for lower throughputs of materials with high vapor pressures at 25°C) were run in a special trap (Figure 5), where the solid hydrocarbon was frozen to the walls of the trap and the carrier gas passed over it. The trap was equipped with teflon stopcocks to keep highly volatile hydrocarbons (like neopentane) without cooling while the system was not in operation, and a bypass to purge the lines of hydrocarbon vapor and prevent F_2 from entering. The valves prevented F_2 from reaching the hydrocarbon in the reservoir after the hydrocarbon carrier was shut off at the end of each run.

A brief explanation of the reaction parameters which are listed in Table 5 is in order. The heading of each of these tables refers to a certain type of reactor system indicated by a capital letter (R through V). The components of each of these reactor systems together with their volumes

TABLE 1

PHYSICAL PROPERTIES OF HYDROCARBONS FLUORINATED IN AEROSOL SYSTEM

Cyclohexane

m.p.: 6.55°C b.p.: 80.74°C

vapor pressure: (see Figure 1 and 2)^{a)}

$$\log_{10} p = 6.8413 - \frac{1201.531}{222.647 + t} \quad p \text{ in [mm]} \\ t \text{ in } [^\circ\text{C}]$$

 C_6H_{12} f.w. = 841,4-Dioxane

m.p.: 11.8°C b.p.: 101.1°C

vapor pressure: (see Figure 1 and 2)^{a)}

$$\log_{10} p = -2316.26/T - 2.77251 \cdot \log T + 16.2007$$

p in [mm] T in [°K]

 $\text{C}_4\text{H}_8\text{O}_2$ f.w. = 88Neopentane

m.p.: -16.6°C b.p.: 9.5°C

vapor pressure: (see Figure 3)^{a)}

$$\text{solid: } \log_{10} p = 7.2034 - \frac{1020.7}{230 + t} \quad p \text{ in [mm]}$$

$$\text{Liquid: } \log_{10} p = 6.60427 - \frac{883.42}{227.782 + t} \quad t \text{ in } [^\circ\text{C}]$$

 C_5H_{12} f.w. = 72

- a) Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds, 1971 (UT, Sci. & Eng. Libr. QD 305 H5W5)

FIGURE 2

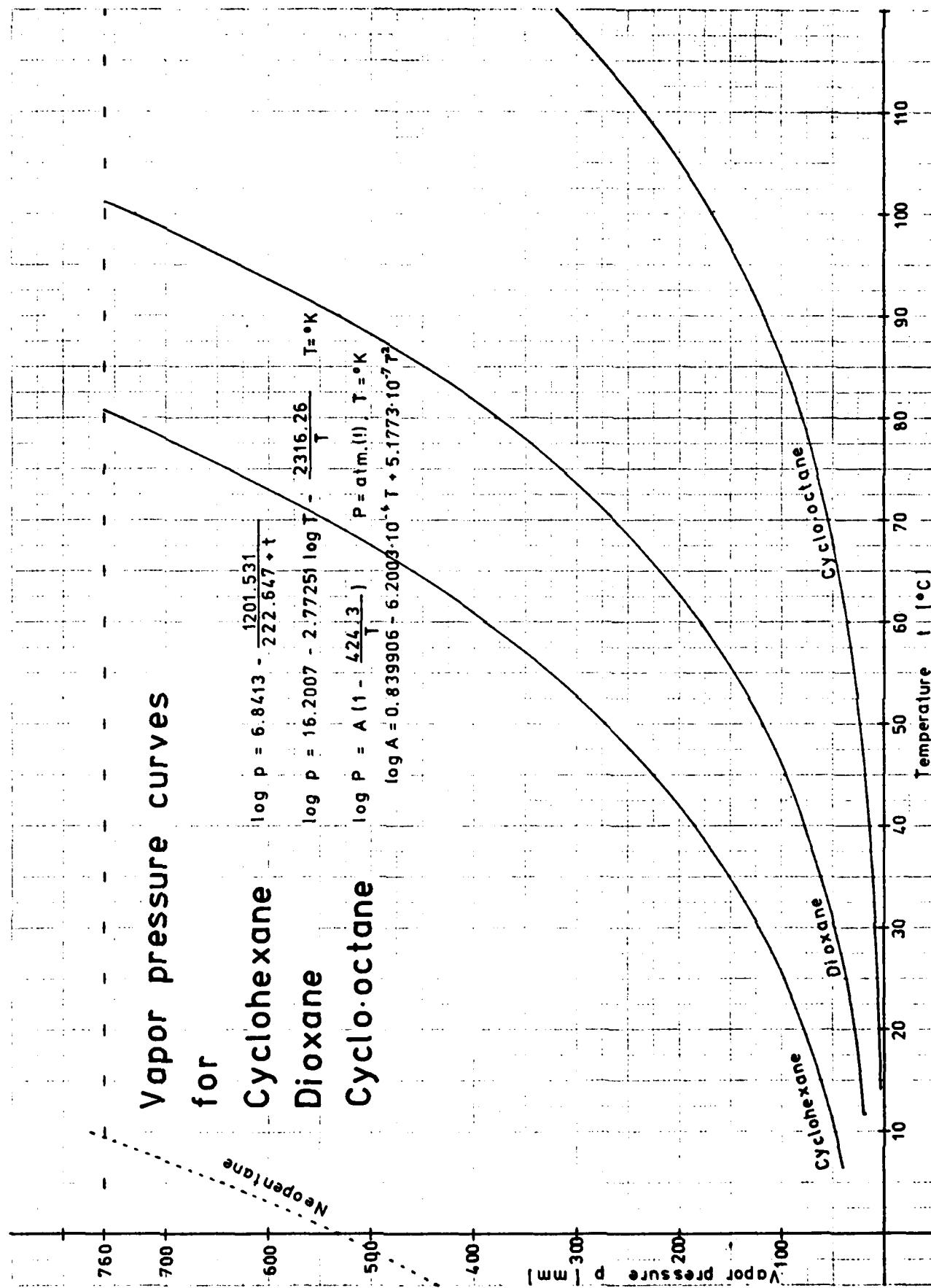


FIGURE 3

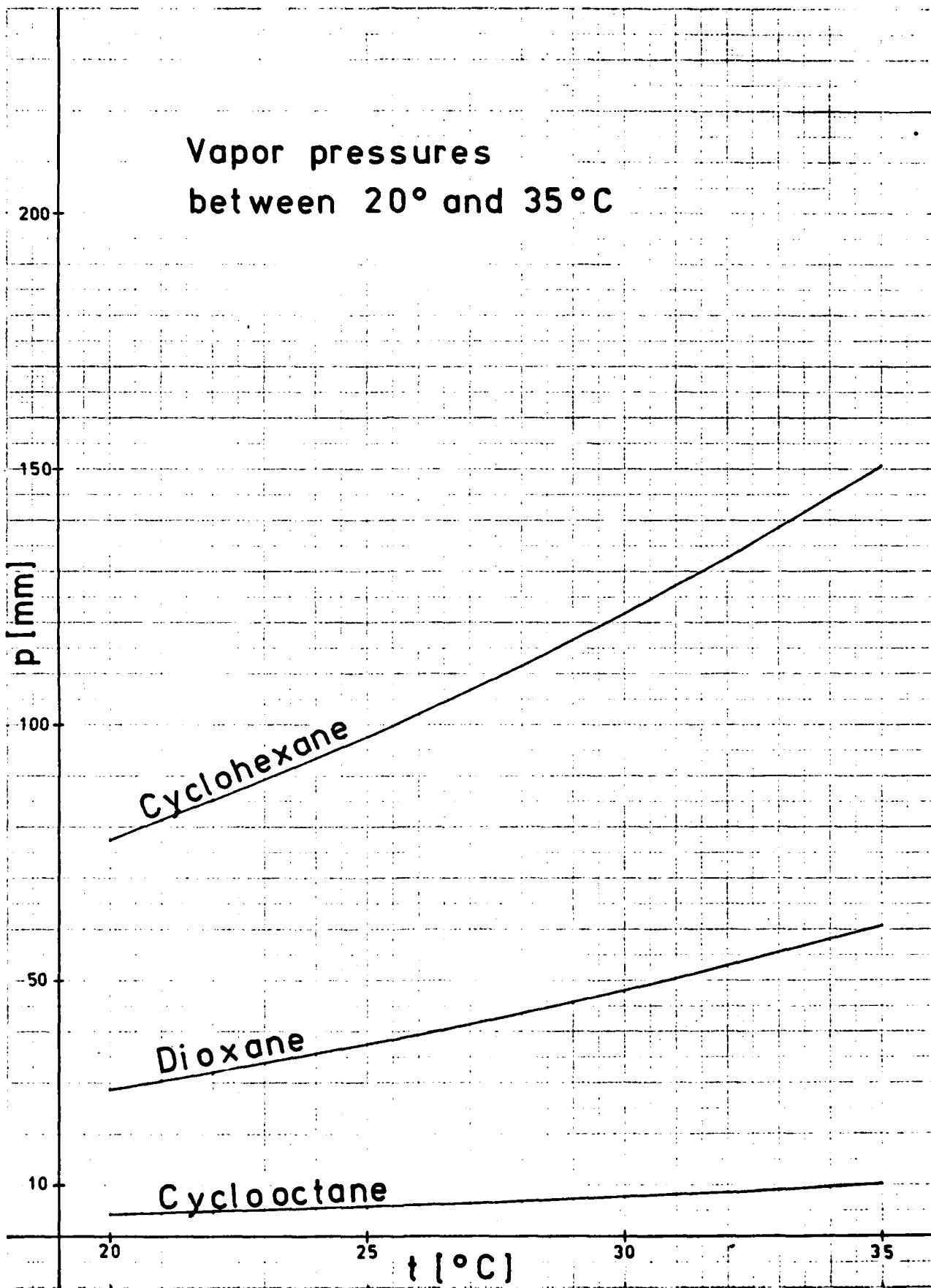
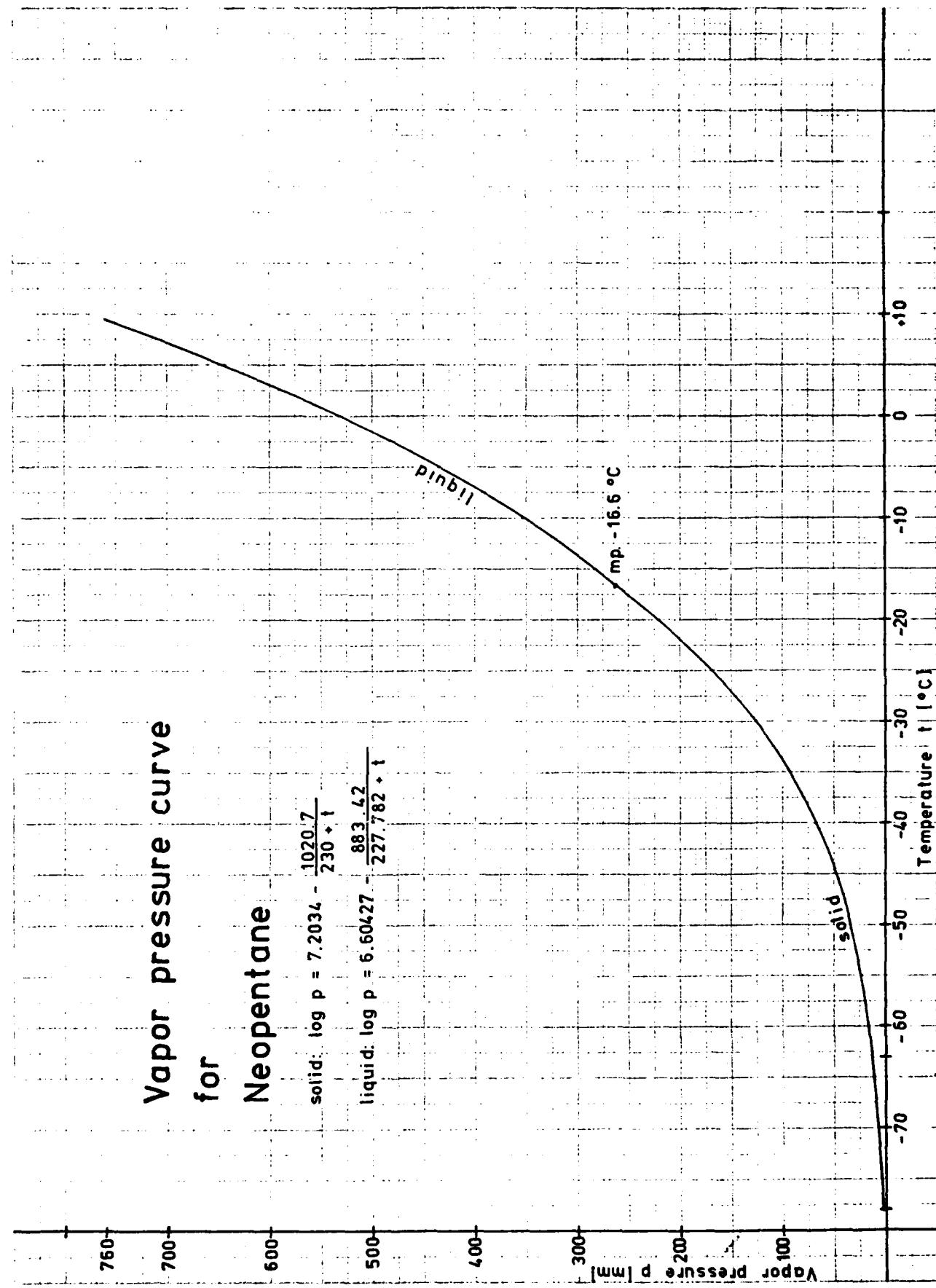


FIGURE 4



0 Millimeters to the Centimeter

TABLE 2
MASS THROUGHPUT FOR CYCLOHEXANE IN AEROSOL SYSTEM

flow-rate ^(a) [cc/min]	mass of C ₆ H ₁₂ [mg/h]	throughput of C ₆ H ₁₂ [mmol/h]
16	390	4.63
24	525	6.24
33	710	8.44
42.5	850	10.10
98.5	2,300	27.33
172	4,100	48.72

(a) mass throughput of cyclohexane versus flow-rate of He through the hydrocarbon reservoir maintained at 30 to 31°C:

flow-rate ^(b) [cc/min]	mass of C ₆ H ₁₂ [mg/h]	throughput of C ₆ H ₁₂ [mmol/hr]
8	60	0.71
14.5	87.3	1.04
43.5	245.8	2.92
102	523.3	6.22

(b) mass throughput of cyclohexane through hydrocarbon reservoir at 0°C:

TABLE 3
MASS THROUGHPUT FOR 1,4-DIOXANE IN AEROSOL SYSTEM

flow-rate ^(a) [cc/min]	mass of C ₄ H ₈ O ₂ [mg/h]	throughput of C ₄ H ₈ O ₂ [mmol/h]
18	188	2.13
25	234.2	2.66
42.5	289.0	3.28
58	421.8	4.79
72.5	492.6	5.59
75	574.2	6.52
97	759.6	8.62
112.5	941.6	10.69
130.5	1,098	12.46
141	1,209	13.72
160	1,361	15.45
174	1,621	18.40

(a) mass throughput of dioxane versus flow-rate of He through hydrocarbon reservoir maintained at 34°C:

flow-rate ^(b) [cc/min]	mass of C ₄ H ₈ O ₂ [mg/h]	throughput of C ₄ H ₈ O ₂ [mmol/h]
52.5	75.8	0.86
63.5	91.1	1.03
101	159.2	1.81

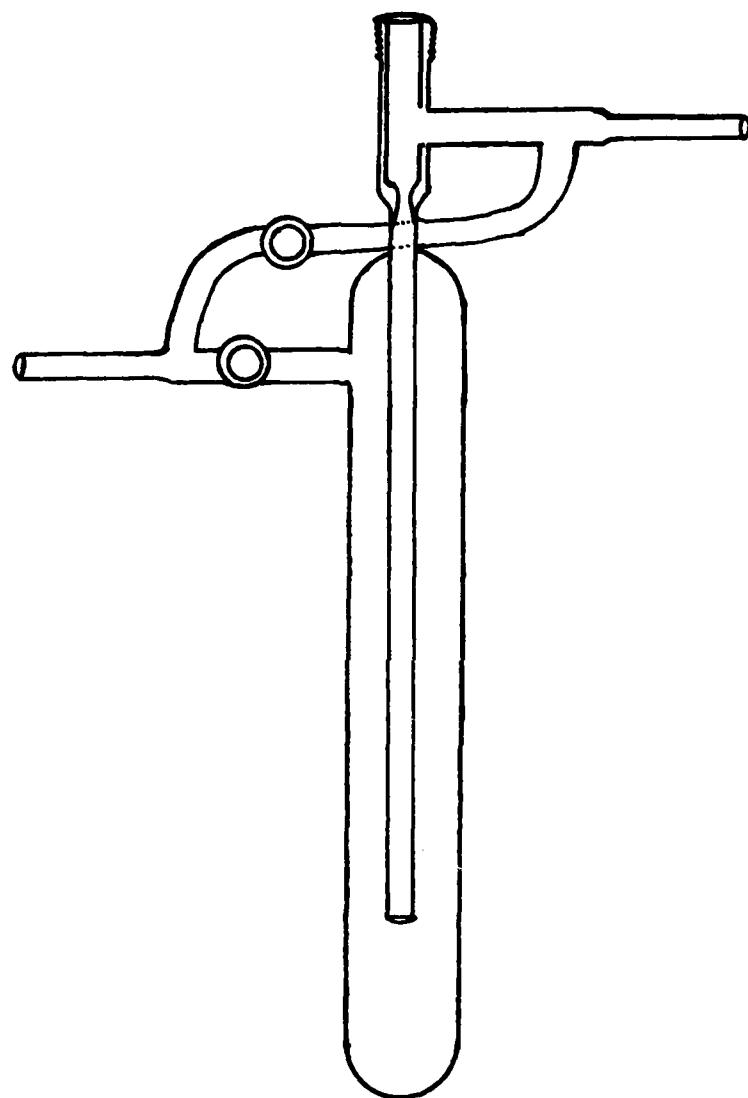
(b) mass throughput of dioxane through hydrocarbon reservoir at 0°C:

TABLE 4
MASS THROUGHPUT FOR NEOPENTANE IN AEROSOL SYSTEM

flow-rate ^(a) [cc/min]	mass of C ₂ H ₁₂ [mg/h]	throughput of C ₂ H ₁₂ [mmol/h]
63.5	38.2	0.53
84.5	60.6	0.84
98	70.8	0.98
100	71.8	1.00
110	94.6	1.31
126	103.4	1.43
174	115.4	1.60

(a) mass throughput of neopentane versus flow-rate of He through the hydrocarbon reservoir maintained at -78°C:

Figure 5.
Hydrocarbon Reservoir for Low Temperatures



are listed below. System R is the single-stage reactor, S the two-stage reactor, and T, U and V are four-stage reactor systems. Volumes of the different reactor systems from aerosol generator to product collecting trap are given as follows:

- R) single stage reactor with 3" F₂-mixing jet and 18" aerosol trap (with dry ice/methanol cooling):

reactor	52.8 cm ³
aerosol trap	225.2 cm ³
tubing + NaF-trap	<u>94.2 cm³</u>
	<u>372.3 cm³</u>

- S) two-stage reactor, reactor plus one module without insert (no aerosol trap):

reactor + short insert	38.5 cm ³
module without insert	156 cm ³
end piece	32.2 cm ³
tubing + NaF-trap	<u>94.2 cm³</u>
	<u>321 cm³</u>

- T) four-stage reactor, reactor plus two modules each with insert:

reactor (as above)	38.5 cm ³
two modules and inserts =	103.6 cm ³
end piece	32.2 cm ³
tubing + NaF-trap	<u>94.2 cm³</u>
	<u>268.5 cm³</u>

- U) four-stage reactor C) + 10m copper coil (8mm i.d.):

C +	<u>502.6 cm³</u>
	<u>771.1 cm³</u>

- V) D) + 15m copper coil: D + 753 cm³
1524.1 cm³

The left part of each table of reaction conditions (e.g. Table 5) lists the experimental values for the different variables used in a given reaction. These are: a) the flow of hydrocarbon, b) the flow of fluorine and c) the flow of inert gas, which consists of the main carrier, the hydrocarbon carrier and the fluorine diluent. Another variable, d) the temperature of the reactor, is only listed in the tables for the multistaging experiments, because it was kept constant at -55° to -60°C in all single-stage fluorination experiments.

The right part of each table lists reaction parameters which were calculated from two or more of the variables previously listed. The hydrocarbon to fluorine (h.c.: F₂) ratio needs no explanation.

The "stoichiometry" listed in the next column(s) is the fluorine-to-hydrocarbon-ratio divided by the number of hydrogens on the hydrocarbon molecule considered. This is more useful than the fluorine-to-hydrocarbon-ratio itself, for example to completely substitute one hydrocarbon molecule with n hydrogen atoms n F₂-molecules are needed for complete fluorination. If different hydrocarbons are compared, the "stoichiometry" gives a better picture of the true reaction conditions than the F₂:h.c.-ratio itself. For example, a 24:1 F₂:h.c.-ratio means a twofold excess of fluorine if cyclohexane or neopentane are considered (stoichiometry = 24:12 = 2), but a threefold excess of fluorine in the case of 1,4-dioxane (stoichiometry = 24:8 = 3).

The next column of each table lists the fluorine concentration for each reaction. This was calculated from the overall fluorine flow divided by the sum of all flows going through the reactor (x100). Thus it represents the concentration one would find at the end of the reactor (in multistaging experiments at the end of module #2), if no reaction would occur. The true fluorine concentration is somewhat lower than this value, the error being

larger for reactions with high hydrocarbon flows and low fluorine flows, while in reactions with low hydrocarbon throughputs and large excess of fluorine the true F_2 -concentration is probably close to the value listed.

In multistaging experiments a gradient in fluorine concentrations was used. For some of the reactions an approximate fluorine concentration profile is given in the diagrams (Figures 6, 7 and 8) for the product distributions of neopentane fluorinations.

The last column of the tables for reaction conditions lists the reaction time. This is the average time a hydrocarbon particle takes to travel from the aerosol generator to the product collecting trap where it is frozen to -196°C and all reaction stops. This time was calculated from the volumes of the various reactor configurations divided by the sum of flows through them. Of course this time is correct only if no hydrocarbon condenses inside the reactor at any time during a run. For the fluorinations of neopentane, especially those with high fluorine concentrations, this assumption is probably correct because of the high volatility of materials involved. The single-stage fluorination reactions of cyclohexane and 1,4-dioxane apparently allowed part of the material to remain in the reactor under conditions in which reaction occurs for a longer time than those listed due to some condensation on the walls of the reactor.

CHRONOLOGICAL DESCRIPTION OF THE DEVELOPMENT OF THE AEROSOL FLUORINATION SYSTEM

Part I

DEVELOPMENT OF A "WORKING" SINGLE-STAGE REACTOR.

The first successful aerosol fluorination reactions of cyclohexane (F/C-1 and F/C-2) as well as unsuccessful attempts to fluorinate 1,4-dioxane (F/D-1 to F/D-4) were described in Technical Report No. 1. The major problem at that time was plugging of the system. It was found in reaction F/C-2,

that warming the chiller to room temperature seemed to solve the initial plugging problems, the chiller was eliminated completely from the system. Plugging then occurred in the tube leading from the generator to the reactor. Reactions F/C-3 through F/C-7 (all with 10 mmoles/h hydrocarbon flow, h.c.:F₂ = 1:1, and 5 l/min main carrier-He) are unsuccessful attempts to solve these later plugging problems with different designs for the connections between aerosol generator and reactor, for example, teflon plugs to thermally insulate the hydrocarbon-aerosol-tube from the cold reactor. Finally the best design proved to be a direct connection between the generator via a monel adaptor and the back of the reactor thus feeding the aerosol directly into the reaction chamber. Because the reactor is maintained at -65°C it was then necessary to heat the generator externally. The temperature best suited for operation of the aerosol generator is different from hydrocarbon to hydrocarbon (e.g. 30°C was used for cyclohexane, 40° for dioxane and 10° to 20° for neopentane).

F/C-8 was the first successful reaction without plugging (10 mmoles C₆H₁₂/h; cyclohexane:F₂ = 1:1; 52/min He). GLC assay showed that the reaction mixture consisted mostly of cyclohexane, some monofluorocyclohexane and small amounts of higher fluorinated materials.

To improve mixing of the hydrocarbon-aerosol and fluorine in the reactor, a short mixing jet was introduced. Reaction F/C-9 showed, that under the same conditions as used previously the amount of monofluorocyclohexane relative to unreacted cyclohexane increased somewhat. In reaction F/C-10 the conditions were as follows: 10 mmoles/h H_2 ; F_2 = 1:4; 5 l/min Helium. The amounts of monofluorocyclohexane and more highly fluorinated materials increased, but still unreacted cyclohexane was the largest peak of the gas chromatogram. The same was true for reaction F/C-11, where the h.c.:F₂-ratio was increased to 1:12. (Reactions F/C-12 and F/C-13 were

repetitions of the 1:1-run and were unsuccessful for unknown reasons.) To further improve mixing of the reactants and reduce the amount of unreacted cyclohexane a new, longer stage one mixing jet was designed. The reactions made with this "final design" of the single-stage reactor (reactor system A) are discussed in detail in the following sections.

Aerosol Fluorination of Cyclohexane in a Single-stage Reactor

Reaction conditions for the fluorinations of cyclohexane are given in Table 5. All reactions (F/C-14 to F/C-20) were run using the single-stage reactor with the long (3") stage one F_2 -mixing jet (R). The reactor temperature was kept constant at -55 to -60°C, the "aerosol trap" equipped with a monel spiral was cooled to -78°C with dry ice/methanol. Products were collected in a trap cooled to -196°C during the reaction and the following warm-up of the reactor and "aerosol trap" over night. Products were then transferred to the vacuum line. Since vacuum fractionation proved only marginally useful, the crude product mixture was condensed into a trap containing NaF-pellets and L-4A molecular sieves to remove HF and water and subjected directly to gas chromatographic separation. The amount of crude product was determined by weighing the NaF/L-4A (sodium fluoride/Linde-4A molecular sieves) trap after the material was condensed into it and weighing it again after the product was condensed back into the vacuum line.

The liquid portion of the products was then injected into the gas chromatograph (column:Fluorosilicone QF-1, 10% on Chromosorb P, 3/8 in. x 7m long; Det./Inj. 160°C, 60 cc/min He flow; the column was kept at a constant temperature of 135°C).

Products from reactions F/C-16 through F/C-19 were separated quantitatively by GLC into fractions A to F. The weights of these fractions for the different reactions are given in Table 6. The sum of these fractional

TABLE 5
REACTION CONDITIONS FOR AEROSOL FLUORINATIONS OF CYCLOHEXANE IN A SINGLE STAGE REACTOR (R) *

*a) A refers to the type of reactor described on page

*b) $F_2 : h.c./12$ - for explanation see text

*c) this is the concentration of fluorine (% vol.) which would be found if no reaction occurred. (F_2 -flow divided by sum of all flows x 100)

*d) this is the approximate time a hydrocarbon particle travels from the aerosol generator to the product collecting trap - assuming that no material condenses inside the reactor system at any time.

TABLE 6

PRODUCT DISTRIBUTIONS FROM CYCLOHEXANE FLUORINATIONS FROM SELECTED AEROSOL FLUORINATIONS

Fraction ^a	Retention time [min]	F/C-16	Material collected [mg]		
			F/C-17	F/C-18	F/C-19
A	7-11	70	35	155	25
B	11-17	80	50	190	80
C	17-23.7	95	140	150	205
D	23.5-29.5	>30	140	140	140
E	29.5-33	150	60	50	160
F	>33		90	50	310
Total c[g]	---	1.46	1.56	1.01	1.49

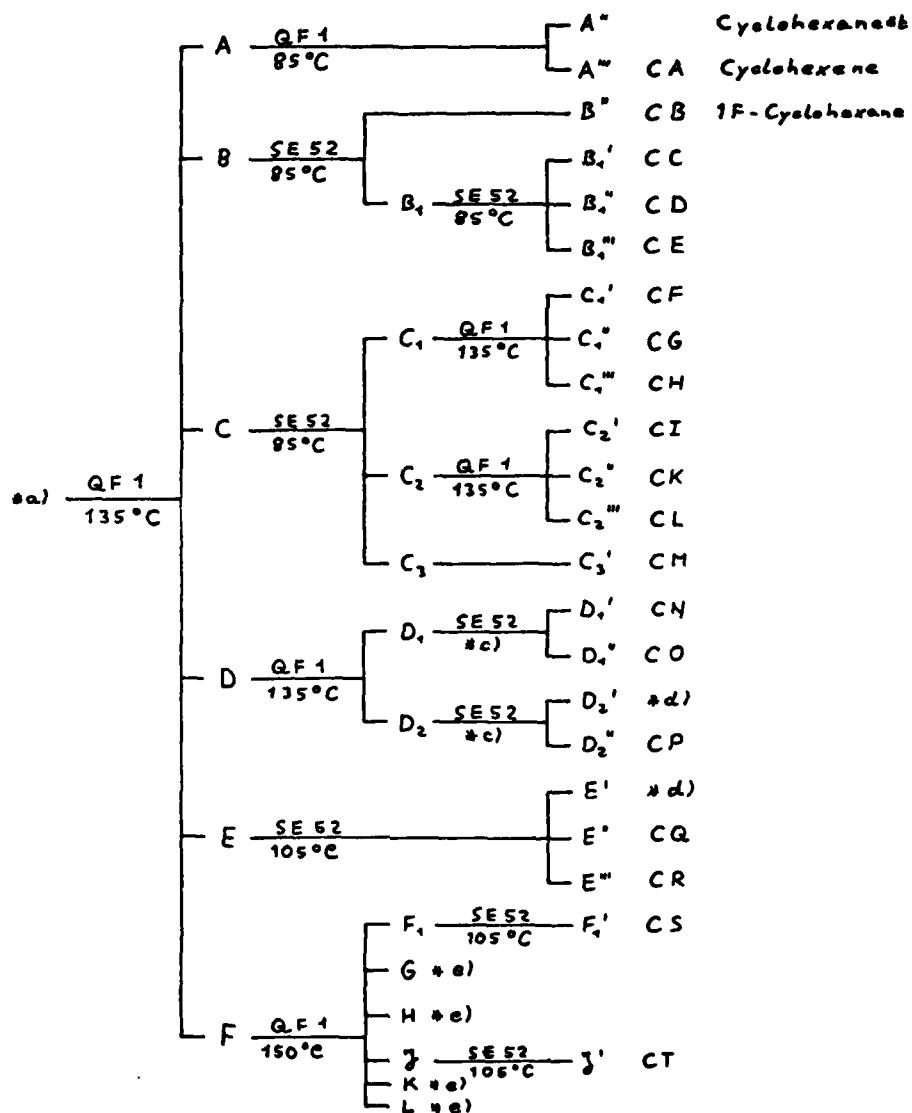
- a) See table 7 for correlation; since fractions from different reactions were combined before further separations, amounts of single compounds for each reaction were not obtained.
- b) Retention times are on QF-1 at 135°C const.; Det./Inj. 160°C; 60 cc/min He flow.
- c) Weight of the crude product mixture after treatment with NaF/molecular sieves before separation.

weights is smaller than the weight of the crude product mixture for several reasons. Part of the material was solid and not soluble in the liquid portion of the product mixture nor was it soluble in solvents like CCl_4 , CHCl_3 , CFCl_3 , acetonitrile or ether. After some time the insoluble solid became involatile (polymerization?). Attempts to take infrared-spectra of this solid in nujol or as KI-pellets failed, so it was not identified. Also part of the material decomposed in the vacuum line leaving solid residues, and some losses are inevitable in GLC-separations in general.

Corresponding fractions for the four reactions (F/C-16 to F/C-19) were combined for further investigations. Later on it was found that all of these fractions consisted of several different compounds, however, the distribution of these products could no longer be related to the initial fractions from each reaction.

Details of the further separation of fractions A to F are given in Scheme 1. The first letter code of each compound directly refers to the fraction this compound was obtained from (e.g. compound C_2''' was obtained from fraction C, subfraction C_2 in a 3rd GLC separation). For easier reference and to avoid confusion a second code consisting of two letters was used. The first letter of this code refers to the parent molecule (here C = cyclohexane), the second letter runs from A to T for subsequent samples.

Scheme 1

SEPARATION OF PRODUCT MIXTURES FROM FLUORINATIONS OF CYCLOHEXANE^{*f)}

- *a) Crude product mixture after treatment with NaF/molecular sieves.
- *b) Unreacted starting material.
- *c) Temperature program: $T_1 = 55^\circ\text{C}$ for 10 min; $R_1 = 10^\circ/\text{min}$; $T_2 = 105^\circ\text{C}$ for 10 min; $R_2 = 30^\circ/\text{min}$; $T_3 = 135^\circ\text{C}$ for 5 min.
- *d) These fractions are still mixtures of minor components; not investigated further.
- *e) These fractions are mixtures of compounds with very low volatilities; using conditions under which reasonable retention times were obtained in other fractions, no satisfying GLC-separations could be achieved. All of fraction F has a retention time greater than 33 min on column QF-1 at 135°C .
- *f) All separations were by GLC on a fluorosilicone QF-1 or silicone rubber SE-52 column as indicated. Conditions: 60 ml/min He flow and detector/inlet at 160°C .

Products from the aerosol fluorinations of cyclohexane after separation and purification by GLC as described earlier were investigated by ^{19}F and ^1H NMR, CI and EI mass spectrometry and by infrared spectroscopy (Table 7).

Proton NMR spectra of partially substituted cyclohexanes are very complex due to conformational changes and extensive coupling across the ring. For these reasons signals appear as broad, not very well resolved, multiplets. It is, however, in general possible to distinguish between protons on CH_2 -groups (which appear between $\delta \approx 1$ to 3 ppm) and protons on CFH -groups, which appear as widely spaced doublets or multiplets between $\delta \approx 3.5$ and 6.5 ppm (due to the large coupling constant, $J \approx 50$ Hz for geminal H-F). The integration ratio of these CFH to CH_2 -groups provides valuable information in determining the degree of fluorination of a given compound.

^{19}F NMR spectra are somewhat more useful because vicinal couplings in many cases are small and not observed. Here, too, signals for F on CF_2 or CFH groups can easily be distinguished, and their relative integrations help to identify the products. The mass spectral data of the partially fluorinated cyclohexanes is much more useful than that for the partially fluorinated neopentanes.

Chemical ionization mass spectra often give the molecular ion minus fluorine ($M-19$) as the most intense peak or at least as one of the more intense peaks. Another relatively intense peak which often appeared is the $M-2\text{F-H}$ peak in the CI mass spectrum. Electron impact (EI) mass spectra in some cases gave a molecular ion; all EI mass spectra contain a large number of lower mass C_nH_x fragments because many of the products obtained in the single-stage fluorination of cyclohexane were not very highly fluorinated (all the compounds investigated still contained CH_2 -groups as determined by ^1H NMR). These low-mass fragments have not been listed for every single compound, because the same fragments appear in most of the spectra with varying intensities.

No attempt has yet been made to completely identify every compound as to what isomer of a given formula and what conformation of what isomer is present. Instead, emphasis has been placed on investigating fluorine substitution because this is the most important factor indicating the efficacy of the aerosol fluorination system under a given set of conditions.

TABLE 7

Infrared; ^1H , ^{19}F NMR and Mass Spectra of Fluorinated Cyclohexanes

CA: A''' = Cyclohexane (comparison with authentic sample)

CB: B'' = Monofluorocyclohexane¹⁴

^{19}F NMR: d at 173.5 ppm Lit.¹⁵ $\phi \approx 175$ ppm.

CC: B₁' Hexafluorocyclohexane isomer

^{19}F NMR

-91.5 ppm

-104.7 ppm

-202.4 ppm

-213.9 ppm

MS: CI: 173 (2.2) $\text{C}_6\text{F}_5\text{H}_6$ (M-F ?); 153 (100) $\text{C}_7\text{F}_4\text{H}_5$ (M-2F-H)

CI: 59 (100) C_3FH_4

IR: 2930 (w), 1490 (s), 1395 (m,br), 1195 (s), 1090 (s),
1055 (s), 960 (w,br), 890 (w,br), 735 (m)

CD: B₁'' Not identified.

$\underline{\text{CH}}_2:\underline{\text{CHF}} \sim 5:1$ (from ^1H NMR)^a

^{19}F NMR: -95.752 ppm $\sim 1:2$

-101.385 ppm

MS: CI: 83 (100) C_6H_{11} , 81 (80.5) C_6H_9

EI: 67 (100) C_5H_7

IR: 3010 (s), 2920 (vs), 2850 (s), 2660 (w), 1650 (w,br),
1450 (m), 1385 (m), 1350 (w), 1270 (m), 1150 (vs),
1125 (m), 1015 (s), 970 (m), 940 (w), 915 (m,sharp),
870 (w), 730 (m), 715 (m,sharp), 700 (w)

^a ^1H NMR of this compound is very similar to cyclohexane, but IR is different, and C_6H_{10} should not give a ^{19}F -NMR spectrum.

TABLE 7 (CONTINUED)

CE: B ₁ '''	1,1-Difluorocyclohexane
	¹ H NMR: only CH ₂ -groups
	¹⁹ F NMR: 95.79 Lit. ¹⁶ $\delta_{CF_2} = 97$ ppm
	MS: CI: 119 (1.5) C ₆ F ₂ H ₉ (M-1), 101 (100) C ₆ HF ₁₀ (M-F)
	EI: 41 (100) C ₃ H ₅
	IR: 2950 (s), 2870 (m), 1450 (m), 1370 (ms), 1290 (ms), 1250 (m), 1160 (m), 1130 (ws), 1025 (mw), 975 (s), 905 (w), 850 (w), 730 (s)
CF: C ₁ '	Trifluorocyclohexane isomer (one CF ₂ , one CFH)
	¹ H NMR: CFH:CH ₂ ~ 1:6
	¹⁹ F NMR: d at 92.6 ppm, d at 104 ppm (both J = 236.5 Hz F-F gem) CF ₂ ; quadruplet at 187.8 ppm CFH; d:d:q ~ 1:1:1
	MS: CI: 119 (100) C ₆ F ₂ H ₉ (M-F), 99 (42.3) C ₆ HF ₈ (M-2F-H)
	EI: 59 (100) C ₃ HF ₄
	IR: 2970 (s), 2880 (w), 1440 (m), 1380 (ms), 1290 (mw), 1240 (m), 1180 (m), 1130 (s), 1045 (m), 995 (s), 915 (mw).
CG: C ₁ ''	Trifluorocyclohexane isomer (one CF ₂ , one CFH)
	¹ H NMR: CFH:CH ₂ ~ 1:6
	¹⁹ F NMR: d at 90.6 ppm both J _{F-F} = 244.1) d at 95 ppm CF ₂ -group t at 199 d:d:t ~ 1:1:1
	MS: CI: 137 (6.7) C ₆ F ₃ H ₈ (M-1), 119 (100) C ₆ F ₂ H ₉ (M-F)
	EI: 55 (100) F ₃ F or C ₄ H ₇
	IR: 2970 (s), 2880 (mw), 1460 (mw), 1380 (s), 1330 (mw), 1310 (mw), 1270 (m), 1240 (mw), 1200 (mw), 1170 (m), 1130 (s), 1035 (vs), 985 (ms), 825 (w)

TABLE 7 (CONTINUED)

CH: C ₁ '''	Difluorocyclohexane (two equivalent CFH groups)
	¹ H NMR CFH:CH ₂ ~ 1:4
	¹⁹ F NMR d at 183.9 ppm J = 53.4 Hz
MS:	CI: 120 (0.2) C ₆ F ₂ H ₁₀ (M), 119 (1.5) C ₆ F ₂ H ₉ (M-1), 101 (99.3) C ₆ FH ₁₀ (M-F), 81 (100) C ₆ H ₉ (M-2F-H)
EI:	120 (8.1) C ₆ F ₂ H ₁₀ (M), 59 (100) C ₃ FH ₄
IR:	2965 (s), 2880 (m), 1460 (w,br), 1390 (w), 1340 (w), 1290 (w), 1160/1155 (mw), 1065 (s), 990 (ms), 900 (mw), 850 (w)
CM: C ₃ '	Mixture
	¹ H NMR CFH:CH ₂ ~ 2:5
	¹⁹ F NMR very complex, seems to be mixture of several compounds
MS:	CI: 175 (13.3) C ₆ H ₆ F ₅ , 155 (66.5) C ₆ F ₄ H ₇ 153 (14.2) C ₆ F ₄ H ₅ , 137 (100) C ₆ F ₃ H ₈ , 117 (68.9) C ₆ F ₂ H ₇
CN: D ₁ '	Mixture
CO: D ₁ ''	Difluorocyclohexane Isomer (two nonequivalent CFH groups)
	¹ H NMR no integration given
	¹⁹ F NMR: d at 175 ppm J _{H-F_{gem}} = 45.8 Hz s at 177.6 ppm d:s ~ 1:1
MS:	CI: 101 (100) C ₆ FH ₁₀ (M-F); 81 (66.4) C ₆ H ₉ (M-2F-H) EI: 120 (13.5) C ₆ F ₂ H ₁₀ (M), 59 (100) C ₃ FH ₄
IR:	2980 (s), 2900 (sh), 1460 (w,br), 1390 (ms), 1290 (br), 1150/1160 (br), 1090 (ms), 1035 (ms), 980 (ms)
CP: D ₂ ''	Difluorocyclohexane isomer (two nonequivalent CFH groups)
	¹ H NMR no integration given
	¹⁹ F NMR d? at 193.5 ppm (J = 106.8 Hz ?)

TABLE 7 (CONTINUED)

MS: CI: 119 (1.4) $C_6F_2H_9$ (M-1), 101 (100) C_6FH_{10} (M-F), 81 (81.2) C_6H_9 (M-2F-H)

EI: 59 (100) C_3FH_4

IR: 2980 (s), 2940 (sh), 2890 (w), 1400 (w), 1300 (w,br), 1220 (w,br), 1150 (w,br), 1100 (s), 1015 (ms), 980 (w), 920 (w,br)

CQ: E'' Tetrafluorocyclohexane isomer (four CFH groups)

1H NMR $CFH:CH_2 \sim 1:2$

^{19}F NMR 4 multiplets centered at 181.1, 183.1 and 185.6 and 191 ppm respectively; rel. integration $\sim 1:1:1:1$

MS: CI: 137 (1.8) $C_6F_3H_8$, 117 (4.9) $C_6F_2H_7$, 101 (8.3) C_6FH_{10} , 99 (100) C_6FH_8

IR: poor because of low vapor pressure of solid compound.

CR: E''' Trifluorocyclohexane (three CFH groups)

1H NMR: $CFH:CH_2 \sim 1:2$

MS: CI: 137 (1.4) $C_6F_3H_8$ (M-1), 119 (79.8) $C_6F_2H_9$ (M-F), 99 (100) C_6FH_8 (M-2F-H)

EI: 138 (0.7) $C_6F_3H_9$ (M) 84 (100) C_5FH_5

^{19}F NMR: d at 186.4 ppm ($J = 45.8$ Hz)

d at 193.6 ppm ($J = 38.1$ Hz) broad s at 206.4 ppm

IR: 2980 (m), 1300 (s,br), 1260 (ms), 1090 (m), 1035 (m), 1000 (s), 960 (ms), 890 (w)

CH: C₁''' Pentafluorocyclohexane isomer (one CF_2 , three CFH)

1H NMR: $CFH:CH_2 \sim 1:2$

^{19}F NMR: d at 106.7 ppm, d at 110 ppm

($J_{FF\text{gem}} = 259.2$ Hz); d at 190.4 ppm ($J_{HF\text{gem}} = 53.4$ Hz)

d at 196.6 ppm ($J = 53.4$ Hz); t at 198.3 ppm

($J = 45.8$ Hz) $CFH:CF_2 = 3:2$

TABLE 7 (CONTINUED)

MS: CI: 174 (0.2) $C_6H_7F_5$ (M); 173 (4.0) $C_6H_6F_7$ (M-1); 155 (100) $C_6H_7F_4$ (M-F); 135 (79.6) $C_6F_3H_6$ (M-2F-H)

EI: 77 (100) $C_3F_2H_3$ or C_6H_5

IR: 2970 (m), 1440 (m), 1400 (m), 1380 (m), 1290 (m), 1200 (m), 1150 (s), 1050 (s), 1020 (m), 880 (w)

CI: C_2'

Difluorocyclohexane isomer (two equivalent CFH groups)

1H NMR $CFH:CH_2 \sim 1:4$

^{19}F NMR s at 186.5 ppm

MS: CI: 119 (1.3) $C_6H_9F_2$ (M-1), 101 (84.1) $C_6H_{10}F$ (M-F), 81 (100) C_6H_9 (M-2F-H)

EI: 120 (2.4) $C_6F_2H_{10}$ (M), 59 (100) C_3FH_4

IR: 2960 (s), 2860 (w), 1450 (m), 1380 (m), 1340 (mw), 1280-1290 (w,br), 1210 (mw), 1150 (mw), 1125 (w), 1070 (m), 970 (s) 840 (mw), 700 (w)

CK: C_2''

Difluorocyclohexane isomer (two equivalent CFH groups)

1H NMR $CFH:CH_2 \sim 1:5$

^{19}F NMR d at 179.8 ppm J = 30.5 Hz

MS: CI: 119 (1.4) $C_6F_2H_9$ (M-1), 101 (100) C_6FH_{10} (M-F)

EI: 120 (3.7) $C_6F_2H_{10}$ (M), 59 (100) C_3FH_4

IR: 2970 (s), 2880 (m), 1460 (mw,br), 1380 (m), 1355 (mw), 1300 (mw), 1130 (m), 1060-1020 (s), 1020/1030 (m), 970 (s), 890 (w), 820 (w), 670 (w), difluorocyclohexane isomer

CS: F_1'

Trifluorocyclohexane isomer (three CFH groups)

1H NMR: $CFH:CH_2 \sim 1:2$

^{19}F NMR d at 181.4 ppm (J = 45.8 Hz), m at ~ 183 ppm, d at 186.1 ppm (J = 53.4 Hz), m at ~ 191.1 ppm; very complex

TABLE 7 (CONTINUED)

MS: CI: 139 (0.4) $C_6F_3H_{10}$ ($M+1$), 119 (85.3) $C_6F_2H_9$
CI: 99 (100) C_6FH_8 ($M-2F-H$)
EI: 59 (100) C_3FH_4

No IR because of low vapor pressure of compound at room temperature.

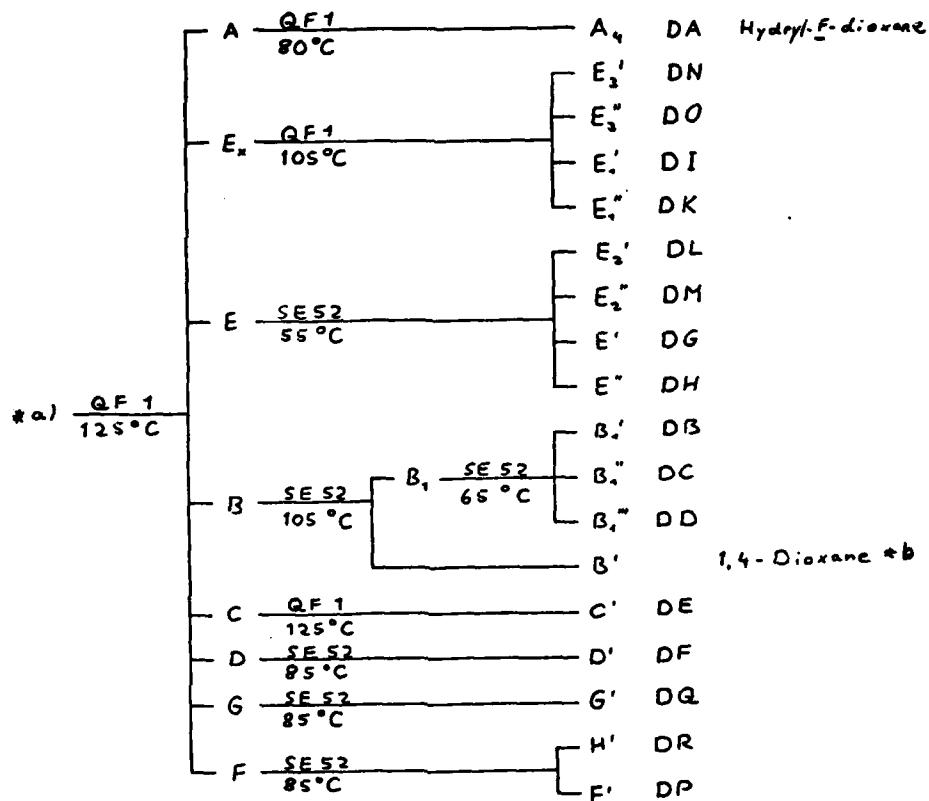
CT: G' Tetrafluorocyclohexane (four CFH groups)
 1H NMR: CFH:CH₂ ~ 1:1
 ^{19}F NMR: s at 184.3 ppm, d at 193.5 ppm (G = 53.4), d at 201.1 ppm (G = 15.2) d at 206.7 ppm (G = 38.1 Hz) equal intensities
MS: CI: 137 (11.7) $C_6F_4H_8$ ($M-F$)
EI: 156 (0.5) $C_6F_4H_8$ (M), 84 (100) C_5FH_5

No IR because of low vapor pressure of compound at 25°C.

Aerosol Fluorination of 1,4-Dioxane in a Single-Stage Reactor

Reaction conditions for the fluorinations of 1,4-Dioxane are given in Table 8. Reactor and procedures were the same as those described previously for cyclohexane. Product mixtures from reactions F/D-5, F/D-6 and F/D-7 were dissolved in CCl_4 and the solutions separated by GLC (column QF-1, 125°C constant), products from reactions F/D-8 to F/D-11 were liquids which could be injected without a solvent. Initial preparative scale separations were divided into fractions A to G. Each of these fractions was further separated (or purified) by GLC under different conditions. For details of those separations see Scheme II. Table 9 lists the product distributions for these reactions. The values given are the weight of each compound collected from the second or third GLC separation (in mg). The distribution in reaction F/D-11 is almost identical to F/D-10 and therefore not listed. In reactions F/D-9, F/D-10 and F/D-11 only fractions with shorter retention times have been separated into single compounds (these are the more highly fluorinated materials); long-retention-time products have been collected together. For latter group yields only the sum is given in the table. Some of the values given may not represent the true product distribution of a given reaction. This discrepancy is due to the fact that some of the lower fluorinated 1,4-dioxanes (especially trifluorides) decompose readily giving brown oily substances and HF. These tend to plug syringe needles and complicate GLC separations. For this reason in later reactions the crude product mixture was left in contact with NaF L-4A molecular-sieves over night. During this treatment most of the unstable materials decomposed and the HF formed was absorbed by the NaF. Thus the original amount of these unstable compounds in some of the product mixtures may have been much higher than that isolated. A second reason for the discrepancy is that the products formed by fluorination of 1,4-dioxane have very different physical

Scheme II

SEPARATION OF PRODUCT MIXTURES FROM AEROSOL FLUORINATIONS OF 1,4-DIOXANE^{*c}

*a) crude product mixture after treatment with NaF/molecular sieves

*b) unreacted starting material

*c) All separations were by GLC on a fluorosilicone QF-1 or silicone rubber SE-52 column as indicated, conditions: 60 ml/min He flow and detector/inlet at 160°C.

TABLE 8
REACTION CONDITIONS FOR AEROSOL FLUORINATIONS OF 1,4-DIOXANE IN A SINGLE STAGE REACTOR (R)

Ref. No.	hydrocarbon flow [mmoles/h]	h.c. carrier [cc/min]	main carrier [cc/min]	F_2 flow [cc/min]	F_2 dil. He flow [cc/min]	reaction time [sec]
				hc: F_2	stoichiometry	% F_2
F/D-5	10	110	5000	4	100	1:1
F/D-5	10	110	5000	16	100	1:4
F/D-7	10	110	5000	32	120	1:8
F/D-8	10	110	5000	96	150	1:24
F/D-9	10	110	3800	64	150	1:16
F/D-10	10	110	2300	64	150	1:16
F/C-11	10	110	3800	96	150	1:24

TABLE 10

DISTRIBUTION OF PRODUCTS FROM AEROSOL FLUORINATIONS OF 1,4-DIOXANE
YIELD (mg) BY REACTION

<u>Product</u>		<u>F/D-5</u>	<u>F/D-6</u>	<u>F/D-7</u>	<u>F/D-8</u>	<u>F/D-9</u>	<u>F/D-10</u>
DA	A ₄					2.6	1.0
DN	E ₃ '	*a)	*a)	*a)	<2.4	6.4	6.1
DO	E ₃ ''				<2.4	9.6	9.4
DI	E ₁ '		1.4	4.1	2.4	7.4	10.1
DK	E ₁ ''	traces		7.5	<2.4	6.3	3.3
DL	E ₂ '		2.8	18.4	14.4	11.6	
DM	E ₂ ''		8.4	36.7	29	27.7	
DG	E'		42.0	105	61.1	~100	
DH	E''		14.1	25.1	18.2	10.8	
DB	B ₁ '			5.2	7.7	4.9	
DC	B ₁ ''		*c)	23.2	19.8	10.3	
DD	B ₁ '''	270 *b)		14.6	9.1	5.8	350
	B'		<5	<5		<1	
DE ^{*d)}	C'		16.2 ^{*d)}	*d)	crude: 60 *d)		
DF	D'			12.4	16.7		
DQ	G'	traces	80	17.7	20.9	190	
DR	H'			11	13.1		
DP	F'		48.3	*) ^e	38.5		
Total *f)[g]				1.18	1.00	0.55	0.62

*a) mixtures from reactions F/D-5, F/D-6 and F/D-7 were injected as solutions in CCl₄. Peaks E₃', E₃'' and part of E₁' (if present in those reactions) lie under the solvent peak.

*b) mostly B' (unreacted dioxane), but some B₁'''.

*c) a mixture of compounds D₁', B₁'' and B₁''' decomposed in vacuum at room temperature over a period of 3 weeks.

*d) this compound has an extremely low volatility; it is difficult to transfer in vacuum, losses are difficult to avoid.

*e) compound F' decomposed in vacuum at room temperature within 3 days.

*f) weight of crude product mixtures after treatment with NaF/molecular sieves before separation. The low values in reactions F/D-9 and F/D-10 may (at least in part) be due to the fact, that these products were left over NaF/molecular sieves over night before weighing. (see text).

properties. Some of the highly fluorinated dioxanes are very volatile liquids with much higher vapor pressures than dioxane itself). The half fluorinated materials, however, are high-melting solids with very low vapor pressures making them difficult to condense into dead volumes (such as storage tubes or ampules). Thus vacuum transfer losses were difficult to avoid. This too leads to a smaller value than that actually present in the original mixtures. Since peaks in the GLC-traces from first separations are overlapping, simple estimation of product distributions from peak areas is not possible. And here, too, distortions due to decomposition of unstable partially fluorinated dioxanes prior to GLC-injection would give false product distributions.

Identification of Products from 1,4-Dioxane Aerosol Fluorinations.

Products from the fluorinations of 1,4-dioxane have been characterized by their ^{19}F and ^1H NMR spectra, CI and EI mass spectra and IR spectra. As in the case of partially fluorinated cyclohexanes, ^1H NMR spectra of partially fluorinated 1,4-dioxanes are very complex due to coupling across the ring. But here, too, signals of CH_2 groups and signals of CFH-groups can be clearly distinguished and their relative integrations give information about the extent of fluorination. ^{19}F NMR spectra are somewhat simpler. In addition a number of ^{19}F NMR spectra for partially fluorinated 1,4-dioxanes (with 4 to 7 F-atoms) have been described in the literature.¹⁷ Burdon and Parsons outline a parameter scheme from which chemical shifts for a fluorine atom of a given conformation of a partially fluorinated 1,4-dioxane may be calculated. Unfortunately, this parameter scheme which works very well for highly fluorinated dioxanes does not fit as well for molecules with more than four hydrogen atoms. In addition, our attempts to apply this scheme to some of the products indicated, that it does not fit well for molecules

with four fluorine atoms if they contain a CH_2 -group, as is the case in several of the products isolated. Thus a complete identification of these products could not be made.

Mass spectra of partially fluorinated 1,4-dioxanes are very useful for identification; EI mass spectra usually show $\text{C}_2\text{F}_n\text{H}_{4-n}$ -masses with very high intensities, from which the number of fluorine atoms on each side of the ring can be determined. ($28 = \text{C}_2\text{H}_4$, $46 = \text{C}_2\text{FH}_3$, $62 = \text{C}_2\text{F}_2\text{H}_2$, $82 = \text{C}_2\text{F}_3\text{H}$, $100 = \text{C}_2\text{F}_4$). In addition to NMR and mass spectra the IR spectra of fluorination products have been listed in Table 10.

TABLE 10

Infrared; ^1H NMR and Mass Spectra of Fluorinated Dioxanes

DA A_4 2-Hydryl-F-1,4-Dioxane*

MS: CI: 215 (6.1) $\text{C}_4\text{O}_2\text{F}_7\text{H}_2$ ($M+1$); 195 (97.3) $\text{C}_4\text{O}_2\text{F}_6\text{H}$ ($M-\text{F}$);
 99 (23.8) $\text{C}_2\text{OF}_3\text{H}_2$; 81 (100) C_2F_3 .
 EI: 100 (100) C_2F_4 ; 69 (32.8) CF_3 , 51 (41.1) CF_2H ;
 50 (20.0) CF_2 ; 47 (18.2) COF ; 31 (18.5) CFH ; 29
 (15.9) COH
 IR: 3010 (vw), 1350 (w), 1300/1290 (s), 1220 (s),
 1200 (s), 1170 (s), 1125 (s), 1100 (m), 1070 (s),
 1025 (sh), 930 (w), 650 (w).

* IR is identical with that of 2-hydryl-F-1,4-dioxane from LTG-fluorinations.

DB: B_4' Mixture of Compounds

^1H NMR: $\text{CFH}:\text{CH}_2 \sim 3:2$
 ^{19}F NMR: $\text{CF}_2:\text{CFH} \sim 1:1$

MS: CI: not consistent, completely different spectra for
 different retention times

EI: 82 (100) $\text{C}_2\text{F}_3\text{H}$; 64 (15.9) $\text{C}_2\text{F}_2\text{H}_2$; 51 (12.4) CF_2H ;
 46 (30.9) C_2FH_3

IR: 3000 (w), 2960 (w), 1280 (s), 1230 (s), 1175 (s),
 1150 (s), 1115/1105 (s), 1080 (s), 970 (w), 910 (w),
 850 (w)

DC: B_1'' Tetrafluoro-1,4-Dioxanes (1 CF_2 , 2 CFH , 1 CH_2 groups)

NMR spectra very complex, perhaps mixture of different isomers
 or conformers

^1H : $\text{CH}_2:\text{CFH} \sim 1:1$
 ^{19}F : $\text{CF}_2:\text{CFH} \sim 1:1$

TABLE 10 (CONTINUED)

IR: 3005 (w), 2970 (w), 1470 (w), 1380 (w,br), 1340 (w),
 1290 (s), 1240 (vs), 1190 (s), 1150 (vs), 1100 (vs),
 1075 (s), 1055 (sh), 1020 (sh), 970 (m), 910 (m),
 850 (w), 820 (w), 680 (w)

DD: B_1''' Trifluoro-1,4-Dioxane (3CFH groups)
 ^1H NMR: $\text{CFH}:\text{CH}_2 \sim 3:2$
 ^{19}F NMR: d at 138.2 ppm ($J_{\text{HF}_{\text{gem}}} = 53.4$ Hz), d at 143.4 ppm
 ($J = 53.4$ Hz), d at 148.2 ppm ($J = 53.4$ Hz) intensity
 ratio $\sim 1:1:1$
 MS: CI: 143 (0.4) $\text{C}_4\text{O}_2\text{F}_3\text{H}_6$ (M+1); 123 (100) $\text{C}_4\text{O}_2\text{F}_2\text{H}_5$
 (M-F); 121 (4.6) $\text{C}_4\text{O}_2\text{F}_2\text{H}_3$; 95 (18.2) $\text{C}_2\text{O}_2\text{F}_2\text{H}$
 EI: 64 (80.1) $\text{C}_2\text{F}_2\text{H}_2$; 47 (12.3) CF0; 46 (100) C_2FH_3 ;
 45 (13.6) C_2FH_2 ; 33 (11.2) CFH₂; 29 (16.6) COH.
 IR: 3000 (mw), 2960 (mw), 1410 (w,br), 1260 (m),
 1220 (s), 1140 (s), 1100 (m), 1040 (vs), 990 (m),
 910 (m), 650 (w).

DE: C' 2,6/3,5-Tetrafluoro-1,4-dioxane; Lit. (Cmpd XII), $\emptyset = 133.0$
 ppm.¹⁷
 ^1H NMR d of multiplets at 5.5 ppm ($J_{\text{HF}_{\text{gem}}} = 53.6$ Hz)
 ^{19}F NMR d at 132.44 ppm ($J_{\text{HF}} = 53.4$ Hz), all F équivalent.
 MS: CI: 141 (40.5) $\text{C}_4\text{O}_2\text{F}_3\text{H}_4$ (M-F); 119 (68.5) $\text{C}_4\text{O}_2\text{F}_2\text{H}$;
 101 (100.0) $\text{C}_4\text{O}_2\text{FH}_2$; 99 (33.7) $\text{C}_4\text{O}_2\text{F}$; 81 (85.0)
 $\text{C}_2\text{F}_2\text{OH}_3$; 59 (96.7) C_2OF .
 EI: 69 (54.9) $\text{C}_3\text{O}_2\text{H}$; 64 (100.0) $\text{C}_2\text{F}_2\text{H}_2$; 59 (24.8) C_2OF ;
 51 (38.9) CF_2H ; 44 (32.8) C_2FH ; 33 (24.4) CFH₂;
 18 (34.5) H_2O

No IR spectrum of the gas was obtained due to the low vapor pressure of the solid.

TABLE 10 (CONTINUED)

DF: D'

Tetrafluoro-1,4-dioxane Isomer, $\text{[O-C}_2\text{F}_3\text{H-O-C}_2\text{F}_3\text{H]}_2$

^1H NMR: $\text{CFH:CH}_2 \sim 1:1$

^{19}F NMR: $\text{CF}_2:\text{CFH} \sim 1:1$.

MS: CI: 161 (0.7) $\text{C}_4\text{O}_2\text{F}_4\text{H}_5$ ($M+1$); 141 (100.0) $\text{C}_4\text{O}_2\text{F}_3\text{H}_4$ ($M-F$)

EI: 82 (100.0) $\text{C}_2\text{F}_3\text{H}$; 46 (93.9) $\text{C}_2\text{F}_3\text{H}_3$.

IR: 3000 (sh), 2980 (mw), 2940 (w), 1460 (w), 1390 (mw), 1360 (sh), 1270/1260 (s), 1220 (vs), 1150 (vs), 1090 (s), 1050 (s), 1030 (sh), 960 (m), 890 (s), 840 (m), 790 (w).

DG: E'

Tetrafluoro-1,4-dioxane Isomer, $\text{[O-CF}_2\text{-CH}_2\text{-O-CFH-CFH]}_2$

^1H NMR: $\text{CFH:CH}_2 \sim 1:1$

^{19}F NMR: $\text{CF}_2:\text{CFH} \sim 1:1$

MS: CI: 141 (100.0) $\text{C}_4\text{O}_2\text{F}_4\text{H}_4$ (M); 64 (100.0) $\text{C}_2\text{F}_2\text{H}_2$

IR: 3005 (mw), 2970 (w), 1460 (w), 1410 (m), 1280 (s,br), 1210 (vs), 1175 (vs), 1110 (w), 1060 (vs), 1030 (vs), 1005 (s), 960 (ms), 915 (m), 865 (m), 790 (w), 650 (w).

DH: E''

2,5/3,6-Tetrafluoro-1,4-dioxane,* Lit. Cmpd. XIV¹⁷

^1H NMR: doublet of multiplets at 5.6 ppm ($J_{\text{HF}_{\text{gem}}} = 56$ Hz)

^{19}F NMR: d at 140.3 ppm ($J_{\text{HF}} = 53.4$ Hz)

MS: CI: 119 (28.8) $\text{C}_4\text{O}_2\text{F}_2\text{H}$; 86 (64.5) C_4OFH_3 ; 84 (100.0) C_4OFH ; 59 (46.2) C_2OF .

EI: 86 (30.9) C_4OFH_3 ; 84 (47.3) C_4OFH ; 82 (47.8) $\text{C}_2\text{F}_3\text{H}$; 64 (100.0) $\text{C}_2\text{F}_2\text{H}_2$

IR: 3000 (w), 2960 (w), 1270 (mw), 1220/1225 (s), 1160 (s), 1130 (m), 1080 (m), 1040 (ms), 1020 (ms), 960 (w), 915 (w), 790 (vw), 660 (w).

TABLE 10 (CONTINUED)

* averaged mixture of 2 equivalent chair-conformations.

DI: E₁'

Pentafluoro-1,4-dioxane Isomer, [O-C₂F₃H-O-CF₂-CH₂]

¹H NMR: CFH:CH₂ ~ 1:2

¹⁹F NMR: CF₂:CFH ~ 3:1 (should be 4:1)

MS: CI: 131 (34.0) C₃OF₄H₃; 101 (28.6) C₂F₄H or C₄O₂FH₂;
82 (32.2) C₂F₃H; 64 (100.0) C₂F₂H₂.

EI: 178 (0.7) C₄O₂F₅O₂ (M); 82 (39.3) C₂F₃H; 64 (100.0)
C₂F₂H₂

IR: 3000 (w), 2960 (w), 1400 (m), 1370 (mw), 1310 (s,br),
1250 (s), 1220 (s), 1195 (s), 1170 (s,br), 1135 (s),
1100 (vs), 960 (ms), 870 (m), 790 (w), 760 (w)

DK: E₁''

2,2,5,5-Tetrafluoro-1,4-dioxane, [O-CF₂-CH₂-O-CF₂-CH₂]

¹H NMR: δ = 4.2 ppm (J = 7.3 Hz)*

¹⁹F NMR: φ = 84.2 ppm,*

MS: CI: 161 (100.0) C₄O₂F₄H₅ (M+1); 159 (44.1) C₄O₂F₄H₃
(M-1); 113 (30.5) C₂O₂F₃; 64 (27.1) C₂F₂H₂

EI: 64 (100.0) C₂F₂H₂

IR: 3005 (vw), 2960 (w), 1460 (w), 1400 (m), 1320 (s),
1260 (s), 1220 (vs), 1140 (s), 1085/1090 (s), 975
(s), 830 (m).

* molecule undergoes rapid inversion, so that all H's and F's
respectively appear equivalent in the NMR.

DL: E₂'

Pentafluoro-1,4-dioxane Isomer; Lit. Cmpd IX¹⁷

¹H NMR: only CFH-groups, no CH₂

¹⁹F NMR: CF₂:CFH ~ 2:3

MS: CI: 109 (30.0) C₃OF₃; 86 (64.3) C₄OFH₃; 84 (100.0)
C₄OFH; 82 (12.7) C₂F₃H

TABLE 10 (CONTINUED)

EI: 178 (0.9) $C_4O_2F_5H_3$ (M); 82 (100.0) C_2F_3H ; 64 (33.2)

$C_2F_2H_2$.

IR: 3000 (w), 2960 (vw), 1400 (w), 1280 (ms), 1250 (m),
1210 (vs), 1170 (s), 1140 (s,br), 1105 (s), 1060 (s),
1020 (ms), 930 (mw), 900 (m), 840 (mw), 690 (mw).

2H,5H-pentafluoro-1,4-dioxane:

	lit.: ¹⁷	comp. E ₂ '
ϕ_{CFH_a})	135.4 ppm	135.1 ppm
ϕ_{CFH_b})	140.2 ppm	139.9 ppm
ϕ_{CFH_c})	150.3 ppm	150.2 ppm
ϕ_{CF_2}	85.3 ppm	85.05 ppm
ϕ_{CF_2}	82.1 ppm	81.7 ppm

DM: E₂'' Pentafluoro-1,4-dioxane Isomer; [0-CF₂CFH-0-CFH-CFH-]

¹H NMR: only CFH-groups, no CH₂

¹⁹F NMR: CF₂CFH ~ 2:3

MS: CI: 109 (100.0) C_3OF_3 ; 107 (20.9) $C_3O_2F_2H$; 86 (37.9)
 C_4OFH_3 ; 84 (59.5) C_4OFH ; 82 (72.7) C_2F_3H ; 64 (27.9)
 $C_2F_2H_2$; 59 (27.6) COF

EI: 178 (0.5) $C_4O_2F_5H_3$ (M); 82 (100.0) C_2F_3H ; 64 (40.8)
 $C_2F_2H_2$

IR: 3000 (w), 1410 (w), 1270 (m), 1230 (vs), 1180 (mw),
1140 (s), 1110 (s), 1060/1050 (s), 925 (w), 900 (m).

DN: E₃' Mixture Dihydryl-F-1,4-dioxanes*, Lit.¹⁷ Cmpds IV, VI, VII.

¹H NMR: only CFH-groups, no CH₂.

¹⁹F NMR: very complex, overall CF₂:CFH ~ 2:1

MS: CI: 197 (0.7) $C_4O_2F_6H_3$ (M+1); 127 (21.6) $C_3O_2F_3H_2$;
101 (100.0) $C_4O_2FH_2$; 82 (53.3) C_2F_3H ; 81 (25.9)
 C_2F_3 ;

TABLE 10 (CONTINUED)

EI: 196 (0.1) $C_4O_2F_6H_2$ (M); 177 (0.2) $C_4O_2F_5H_2$ ($M-F$);

82 (100.0) C_2F_3H 51 (22.4) CF_2H

IR: 3000 (vw), 1390 (w), 1290/1300 (ms), 1240 (s),
1210 (s), 1150 (s), 1120 (vs), 1080 (ms), 905 (m),
790 (m).

from comparison of ^{19}F NMR with the literature,¹⁷ this is a mixture of three different hexafluoro-1,4-dioxanes:
2H,6H-/hexafluoro-1,4-dioxane, 2H/5H-hexafluorodioxane and 2H,5H-hexafluoro-1,4-dioxane.

DO: E₃"

Pentafluoro-1,4-dioxane Isomer; $\boxed{O-C_2F_3H-O-CF_2-CH_2}$

^{19}F NMR: $CF_2:CFH \sim 4:1$

1H NMR: $CFH:CH_2 \sim 1:1$

MS: CI: 131 (100.0) $C_3OF_4H_3$; 64 (17.0) $C_2F_2H_2$

EI: 82 (43.3) C_2F_3H ; 64 (100.0) $C_2F_2H_2$

IR: 3000 (vw), 2960 (vw), 1300 (ms), 1260 (ms), 1185
(vs), 1120 (s), 1060 (s), 975 (mw), 930 (w), 855
(mw), 650 (w).

DP: F;

Trifluoro-1,4-dioxane Isomer; $\boxed{O-CFH-CFH-O-CFH-CH_2}$

1H NMR: $CFH:CH_2 \sim 3:2$

^{19}F NMR: only CFH-groups, no CF_2

no MS, because material decomposed rapidly: IR poor because of low vapor pressure of compound: 2960 (w,br), 1270 (mw,br), 1220 (s), 1110 (s), 1010-1055 (s,br), 935 (m), 895 (w), 875 (w).

DQ: G'

Tetrafluoro-1,4-Dioxane Isomer (1CF₂, 2CFH, 1CH₂)

1H NMR: $CFH:CH_2 \sim 1:1$

^{19}F NMR: $CF_2:CFH \sim 1:1$

TABLE 10 (CONTINUED)

MS: CI: 101 (18.7) $C_4O_2FH_2$; 86 (64.2) C_4OFH_3 ; 84 (100) C_4OFH
 EI: 86 (62.6) C_4OFH_3 ; 84 (100.0) C_4OFH ; 49 (35.4) $COFH_2$;
 47 (44.9) COF ;
 IR: 2970 (w), 1460 (w), 1390 (w), 1360 (w), 1300 (ms),
 1250 (s), 1160 (s), 1130 (m), 1100 (s), 1040/1050 (s),
 920/930 (m), 885 (mw), 860 (w).

DR: H^t

Mixture

¹H NMR: $CFH:CH_2$ ~ 3.2, very complex¹⁹F NMR: $CF_2:CHF$ ~ 1:3, very complexMS: CI: 141 (69.8) $C_4O_2F_3H_4$; 123 (100.0) $C_4O_2F_2H_5$ EI: 64 (100.0) $C_2F_2H_2$ IR: poor due to low vapor pressure 2990 (w), 1220 (s),
 1180 (s), 1120 (m), 1085 (m), 1050 (ms), 1030 (ms),
 895 (m), 830 (w).

Part II

MULTISTAGING EXPERIMENTS: A DYNAMIC CONCENTRATION GRADIENT, TEMPERATURE GRADIENT AEROSOL REACTOR

THE AEROSOL FLUORINATION OF NEOPENTANE.

Neopentane was chosen as model compound for the multistaging experiments for several reasons:

- i) Partially fluorinated neopentanes should be stable, since α -elimination of HF, which is very favourable in partially fluorinated dioxanes, cannot occur; β -elimination of HF to form a 3-membered ring should not occur under work-up conditions.
 - ii) Partially fluorinated neopentanes should have a higher volatility and solubility than similar cyclohexanes, thus facilitating work-up and giving a true product distribution.
 - iii) there are not as many different isomers and no different conformations for a given degree of fluorination. Therefore the influence of reaction parameters should be more easily seen directly from the product distribution. In addition, GLC separation in one step should be possible, so that the GLC-chromatogram can be used for quantitative estimation of product distributions (Figure 6).
 - iv) Four of the most highly fluorinated neopentanes (i.e. F-neopentane, undecafluoroneopentane, decafluoroneopentane and nonafluoroneopentane) have been identified from low temperature gradient (LTG) fluorination reactions, thus making it easier to judge the "success" of a fluorination.
- The results of the experiments confirmed that neopentane is indeed a very good model substance to test the influence of reaction conditions on the product distribution.
- Reactions F/N-1 to F/N-7 were run in a two-stage reactor system (S). The reactor with stage one jets was fitted with a staging insert which resulted in both fluorine flows going into the reactor, a module without insert

followed, followed by an end cap adaptor instead of the "aerosol trap" of the one-stage reactor. Table 11 lists the reaction conditions for these fluorinations. For all seven reactions the temperature of the reactor was -65°C, that of the module was -60°C. No reactions with less than the stoichiometric amount of fluorine (i.e. 12 F₂ per C₅H₁₂) were run since no perfluorination should be expected under such conditions.

Since none of the known highly fluorinated neopentanes was formed in these reactions, a fluorine insert was added to the first module and a second module with fluorine insert was added to the reactor system. A four-stage reactor (T) was thus formed. Reactions F/N-8 to F/N-12 were run with this extended reactor system. Table 12 gives the reaction conditions for these reactions.

To increase the volume of the reactor and thus the reaction time, a 10 m copper coil (i.d. 8mm) was coupled to the end cap following module #2 (reactor system U). This reactor system was used for the rest of the neopentane fluorinations (F/N-13 to F/N-21), which are listed in Table 13. Product mixtures from all neopentane fluorinations were treated with NaF/molecular sieves (as described for cyclohexane fluorination products). To check the performance of every reaction, an analytical GLC-injection of a solution of the product mixture in CCl₄ was made on the 15% fluorosilicone QF-1 column. The temperature program used is the same as for product separations from LTG-neopentane fluorinations: T₁ = 25°C for 10 min; R₁ = 10°/min; T₂ = 75°C for 10 min; R₂ = 50°/min; T₃ = 125°C for 24 min.

To identify the unknown partially fluorinated neopentanes, products from reactions F/N-1, 11, 14, 17, 18 and 19 were separated preparatively by GLC to obtain samples for NMR-measurements. Corresponding products from reactions F/N-2, 4, 5 and 13 were separated for mass spectral investigations.

Identical samples from the different reactions (as certified by IR) were

TABLE 11
REACTION CONDITIONS FOR AEROSOL FLUORINATIONS OF NEOPENTANE IN A TWO-STAGE REACTOR (S)

Ref. No.	hydrocarbon flow [mmoles/h]	h.c. carrier [cc/min]	main carrier [cc/min]	F ₂ -flow		F ₂ dil. He flow [cc/min]	hc:F ₂	stage 1	stoichiometry at end of time	% F ₂ reactors. [sec]	reaction time
				st. 1	st. 2						
F/N-1	1	101	5000	5	-	5	100 + 20	1:12	1 - 1	0.1	3.7
F/N-2	1	101	2500	5	-	5	20 + 20	1:12	1 - 1	0.19	7.3
F/N-3	1	101	2500	10	-	10	20 + 20	1:24	2 - 2	0.38	7.3
F/N-4	1	101	2500	5	5	10	20 + 20	1:24	1 1 2	0.38	7.3
F/N-5	1	101	2500	5	15	20	20 + 20	1:48	1 3 4	0.75	7.2
F/N-6	1	101	2500	20	-	20	20 + 20	1:48	4 - 4	0.75	7.2
F/N-7	1	101	2500	20	20	40	20 + 20	1:96	4 4 8	1.5	7.2

TABLE 12

REACTION CONDITIONS FOR AEROSOL FLUORINATIONS OF NEOPENTANE IN A FOUR-STAGE REACTOR (T)

Ref. No.	hydrocarbon	h.c. carrier [cc/min]	main carrier [cc/min]	F ₂ -flows [cc/min]				F ₂ dil He flow [cc/min]	
	flow [mmoles/h]			stage 1	2	3	4		
F/N-8	1	101	2500	20	20	-	-	40	4 x 20
F/N-9	1	101	2500	20	20	20	-	60	3 x 20 + 10
F/N-10	1	101	2500	20	20	20	20	80	4 x 20
F/N-11	1	101	2500	20	20	20	20	80	4 x 20
F/N-12	1	101	2500	20	20	20	20	80	4 x 20

continued below

Ref. No.	hc:F ₂	stoichiometry in stage				Σ	% F ₂ at end of react. syst.	reaction time [sec]	temperature [°C] modules		
		1	2	3	4				reactor #1	#2	
F/N-8	1:96	4	4	-	-	8	1.5	5.9	-65	-60	-60
F/N-9	1:144	4	4	4	-	12	2.2	5.9	-65	-60	-60
F/N-10	1:192	4	4	4	4	16	2.9	5.8	-65	-60	-60
F/N-11	1:192	4	4	4	4	16	2.9	5.8	-65	-60	-30
F/N-12	1:192	4	4	4	4	16	2.9	5.8	-65	-60	-30

TABLE 13

REACTION CONDITIONS FOR AEROSOL FLUORINATIONS OF NEOPENTANE IN A FOUR-STAGE REACTOR + COPPER COIL (U)

Ref. No.	hydrocarbon flow	h.c. carrier	main carrier	F ₂ flows [cc/min]					F ₂ dil. He flow	[cc/min]
	[mmoles/h]	[cc/min]	[cc/min]	in stage	1	2	3	4	Σ	
F/N-13	1	101	2500	20	20	20	20	80	4 x 20	
F/N-14	1	101	2500	20	20	20	20	80	4 x 20	
F/N-15	1	101	2500	20	20	20	20	80	4 x 20	
F/N-16	1	101	1250	20	20	20	20	80	4 x 20	
F/N-17	1	101	600	20	20	20	20	80	4 x 10	
F/N-18	1	101	600	20	20	40	40	120	4 x 5	
F/N-19	1	101	600	20	20	60	60	160	4 x 10	
F/N-20	1	101	400	20	20	60	100	200	4 x 5	
F/N-21	4	101	400	20	20	60	100	200	4 x 5	

Ref. No.	temperature [°C] modules				hc:F ₂	stoichiometry in stage					% F ₂	reaction time [sec]
	reactor	#1	#2	coil		1	2	3	4	Σ		
F/N-13	-65	-60	-30	RT	1:192	4	4	4	4	16	2.9	16.8
F/N-14	-65	-30	0	+45	1:192	4	4	4	4	16	2.9	16.8
F/N-15	-65	-30	0	+45	1:192	4	4	4	4	16	2.9	16.8
F/N-16	-65	-30	0	+45	1:192	4	4	4	4	16	5.3	30.6
F/N-17	-65	-30	0	+45	1:192	4	4	4	4	16	9.7	56.3
F/N-18	-65	-30	0	+45	:288	4	4	8	8	24	14.3	55
F/N-19	-65	-30	0	+45	1:384	4	4	12	12	32	17.25	51.3
F/N-20	-65	-30	0	+45	1:480	4	4	12	20	40	27.7	64.1
F/N-21	-65	-30	0	+45	1:120	1	1	3	5	10	27.7	64

combined in order to get enough material for spectral investigations, since every reaction (with a hydrocarbon flow of 1 mmole/h and 2 hours run time) gave between 100 and 300 mg of crude product mixture.

Only one fraction from the first GLC-separations was further separated. It is the peak between 33 and 35 min retention time (Figure 6), which was separated on a 3m 10% phenylmethylsilicone, SE-52 column with the following temperature program: $T_1 = 70^\circ\text{C}$ for 10 min; $R_1 = 25^\circ/\text{min}$; $T_2 = T_3 = 120^\circ\text{C}$ for 7 min.

The product distributions for some typical reactions were estimated by determining the areas of peaks in the GLC-traces. The reactions chosen for this were: F/N-1, F/N-6, F/N-7, F/N-11, F/N-16, F/N-17, F/N-20 and F/N-21. Table 14 lists these product distributions. Since no decomposition during work-up was observed, and all materials were volatile and soluble in CCl_4 , and CFCl_3 , these values should represent something close to the real product distribution for the neopentane fluorinations under different reaction conditions. Thus these distributions could be used to graphically show the effect of reaction parameters on fluorination efficiency (Figure 7).

Identification of Products From Neopentane Aerosol Fluorinations.

Products from the aerosol fluorinations of neopentane were identified on the basis of their ^{19}F and ^1H -NMR spectra, CI and EI mass spectra and IR spectra. Assignments are based mainly on the NMR spectra, because the chemical shifts for fluorines as well as hydrogens on the differently fluorinated methyl groups (i.e. CH_3 , CH_2F , CHF_2 , CF_3) are very characteristic; their couplings are relatively simple, and integrations also help to clearly identify products. ^{19}F NMR spectral data are listed in Table 15, ^1H NMR spectra in Table 16. The previously known data for the highly fluorinated neopentanes (from LTG reactions) have been included for comparison.

Figure 6

Neopentane Product Distributions by GLC Retention Times.

Neopentane Product Distributions - GLC

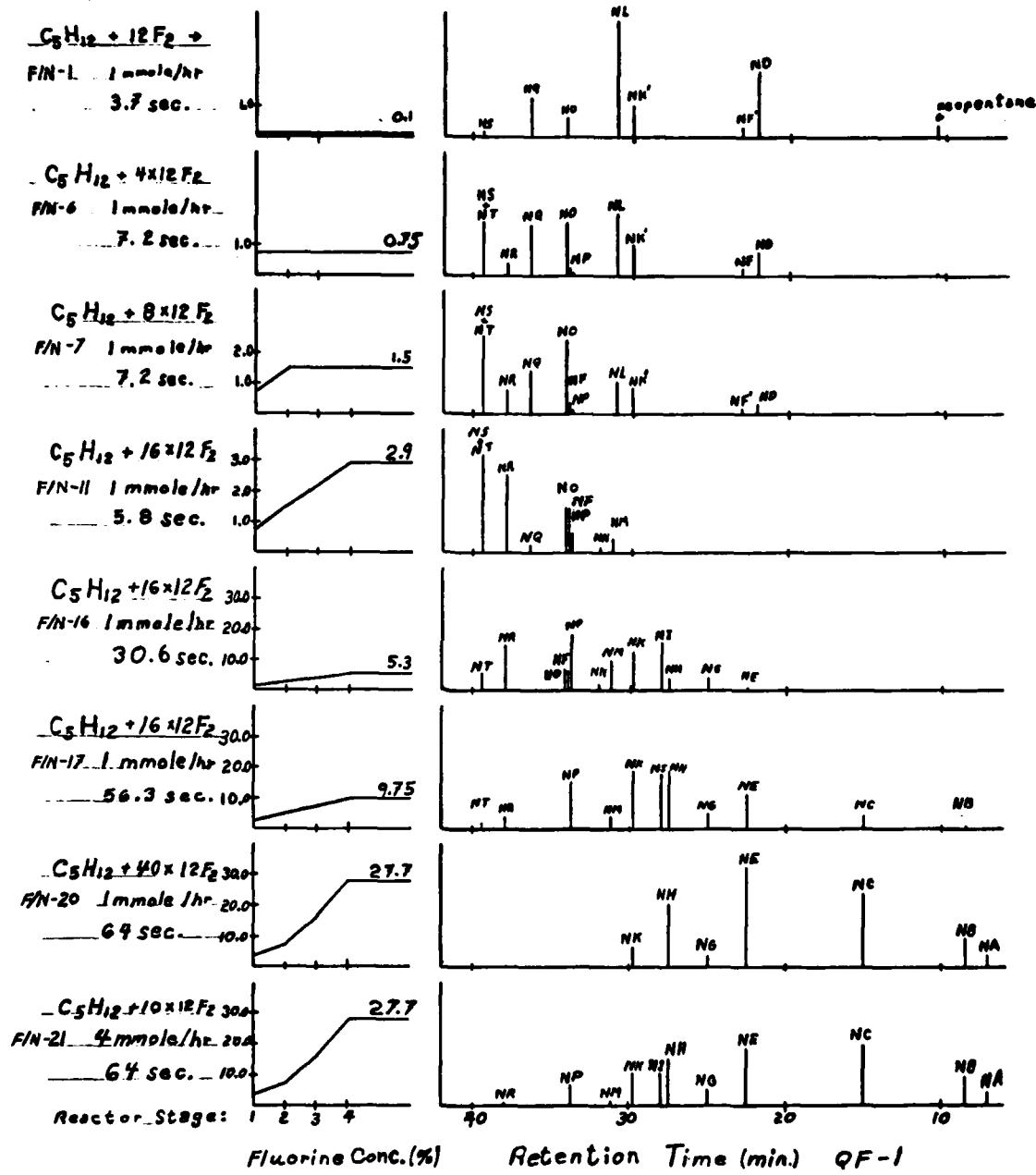


TABLE 14

% PRODUCT DISTRIBUTIONS FROM SELECTED AEROSOL FLUORINATIONS OF NEOPENTANE
(ESTIMATED FROM PEAK AREAS OF GLC-TRACES)

	F/N-1	F/N-6	F/N-7	F/N-11	F/N-16	F/N-17	F/N-20	F/N-21
*	4.0	0.5	0.3		* = unreacted neopentane			
NA					0.3	4.0	4.0	
NB					0.6	9.2	9.0	
NC					4.4	24.0	19.4	
ND	21.8	7.6	3.2					
NE					0.7	11.2	32.6	18.6
NF'	4.3	2.5	1.6					
NG					4.1	5.1	3.3	5.0
NH					3.9	18.9	20.8	14.7
NI					15.7	17.4		10.3
NK'	10.7	10.1	8.7					
NK					12.4	18.7	6.2	10.2
NL	37.9	20.1	10.3					
NM					4.6	9.6	3.5	1.5
NN					1.6	1.5		
NO	6.5	17.4	23.9	14.7	7.4			
NF		2.8	3.8	14.3	6.4			
NP		0.9	1.3	6.1	18.1	15.2		6.5
NQ	12.8	16.2	14.0	2.2				
NR		4.1	7.6	24.7	14.9	3.5		0.7
NS	1.8	(3.6)	(5.1)					
		17.8	25.3					
NT		(14.2)	(20.2)	31.8	5.3	1.3		

FIGURE 7
NEOPENTANE PRODUCT DISTRIBUTIONS

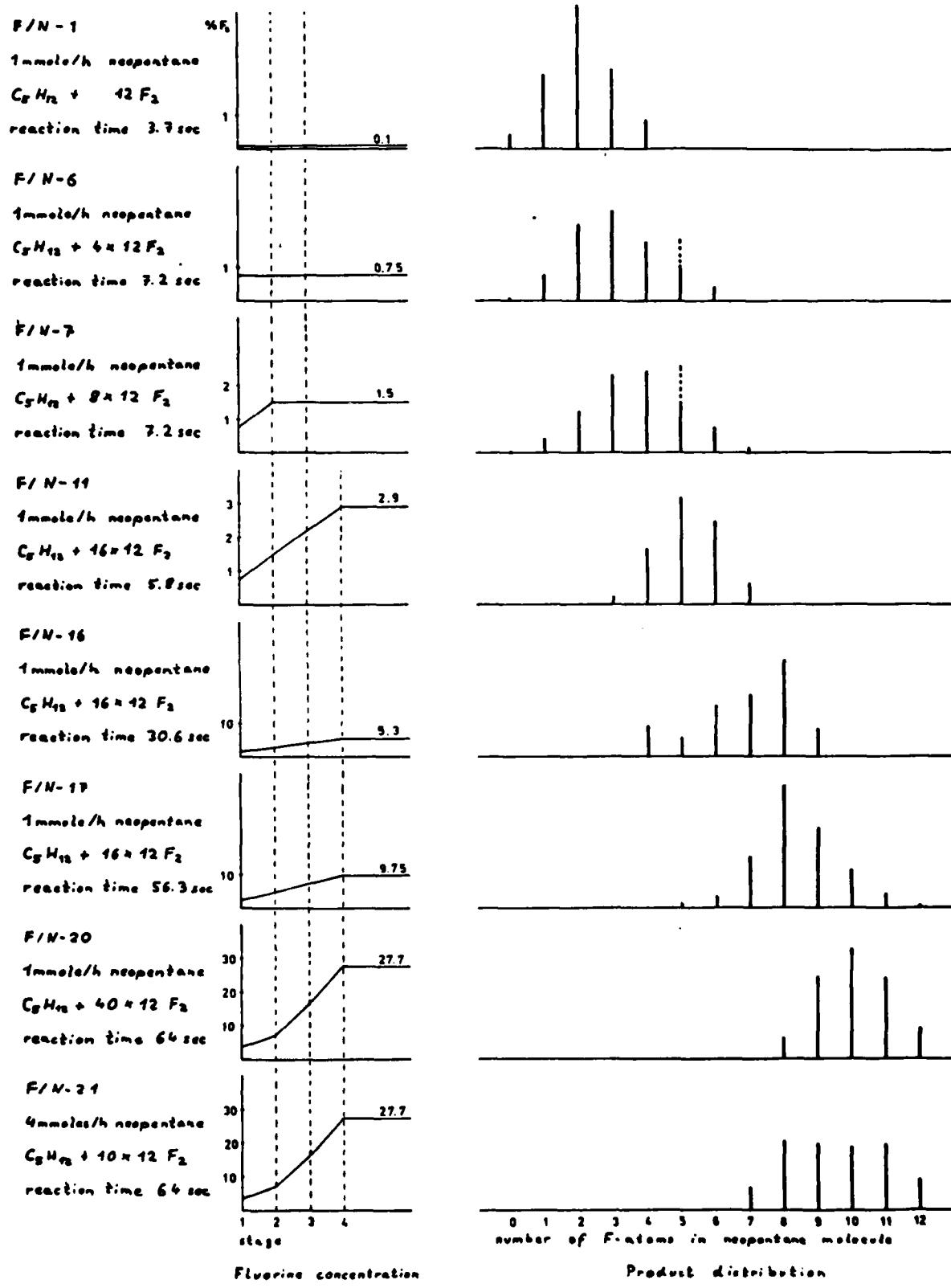


TABLE 15
 ^{19}F NMR DATA OF FLUORINATED NEOPENTANES

Formula	Ref. No.	Structure	δ [ppm] a)	J [Hz]	δ [ppm] a)	J [Hz]	δ [ppm] a)	J [Hz]	δ [ppm] a)	J [Hz]	Integration ratios
C_5H_{12}	*	$\text{C}(\text{CH}_3)_4$									
$\text{C}_5\text{H}_{11}\text{F}$	ND	$(\text{CH}_3)_3\text{C}-\text{CFH}_2$									
$\text{C}_5\text{H}_{10}\text{F}_2$	NL	$(\text{CH}_3)_2\text{C}(\text{CFH}_2)_2$									
$\text{C}_5\text{H}_9\text{F}_2$	NP ^b	$(\text{CH}_3)_3\text{C}-\text{CF}_2\text{H}$									
$\text{C}_5\text{H}_8\text{F}_3$	NQ	$(\text{CFH}_2)_3\text{C}-\text{CH}_3$									
$\text{C}_5\text{H}_7\text{F}_3$	NK ^b	$(\text{CH}_3)_2\text{C}(\text{CFH}_2)(\text{CF}_2\text{H})$									
$\text{C}_5\text{H}_6\text{F}_4$	NS	$\text{C}(\text{CFH}_2)_4$									
$\text{C}_5\text{H}_5\text{F}_4$	NN	$(\text{CH}_3)_2\text{C}(\text{CF}_2\text{H})_2$									
$\text{C}_5\text{H}_4\text{F}_4$	NO	$(\text{CFH}_2)_2\text{C}(\text{CF}_2\text{H})(\text{CH}_3)$									
$\text{C}_5\text{H}_3\text{F}_5$	NT	$(\text{CFH}_2)_3\text{C}-\text{CF}_2\text{H}$									
$\text{C}_5\text{H}_2\text{F}_5$	NR	$(\text{CFH}_2)_2\text{C}(\text{CF}_2\text{H})_2$									
$\text{C}_5\text{H}_1\text{F}_7$	NP	$(\text{CF}_2\text{H})_3\text{C CFH}_2$									
$\text{C}_5\text{H}_4\text{F}_8$	NK	$\text{C}(\text{CF}_2\text{H})_4$									
$\text{C}_5\text{H}_3\text{F}_8$	NI	$(\text{CF}_2\text{H})_2\text{C}(\text{CF}_3)(\text{CFH}_2)$	66.8	(s)	129.3	(d)	51	244.4	(t)	41	$s:d:t = 3:4:1$
$\text{C}_5\text{H}_2\text{F}_9$	NH	$(\text{CF}_2\text{H})_3\text{C}-\text{CF}_3$	64.5	(s)	127.8	(d)	51				$s:d \approx 1:2$
$\text{C}_5\text{H}_1\text{F}_9$	NG	$(\text{CF}_3)_2\text{C}(\text{CFH}_2)(\text{CF}_2\text{H})$	67.33 ^c	(q)	130.1 ^c	(d)	52.2	240.4 ^c	(t)	45.6	
$\text{C}_5\text{H}_2\text{F}_{10}$	NE	$(\text{CF}_2\text{H})_2\text{C}(\text{CF}_3)_2$	64.6 ^c	(p)	127.29	(d)	54.5				
C_5HF_{11}	NC	$(\text{CF}_3)_3\text{C}-\text{CF}_2\text{H}$	65.4 ^c	(t)	125.7		53				
C_5F_{12}	NB	$\text{C}(\text{CF}_3)_4$	65.42 ^c	(s)							

a) Chemical shifts δ [in ppm] are relative to internal CFCl_3 ; since resolution of the spectra was not very high, only the large geminal F-H couplings were observed.

b) Chemical shift values measured from spectra.

c) Data from LiG-products, chemical shifts are measured from spectra.

TABLE 16

 ^1H NMR SPECTRA OF FLUORINATED NEOPENTANES^{a)}

Formula	Ref. No.	Structure	δ [ppm]	CH_3 [Hz]	$\text{J}^{\text{b)}$	CH_2F [ppm]	δ [Hz]	CHF_2 [ppm]	δ [Hz]	$\text{J}^{\text{b)}$ [Hz]	Integration Ratios
$\text{C}_5\text{H}_{12}^{\text{d)}$	*	$\text{C}(\text{CH}_3)_4$	0.94								
$\text{C}_5\text{H}_{11}\text{F}$	ND	$(\text{CH}_3)_3\text{C}-\text{CFH}_2$	0.96	(d) 1.7	4.0	(d) 4.8					
$\text{C}_5\text{H}_{10}\text{F}_2$	NL	$(\text{CH}_3)_2\text{C}(\text{CFH}_2)_2$	0.96	(t) 1.8	4.2	(d) 47.6					
$\text{C}_5\text{H}_{10}\text{F}_2$	NF ^{e)}	$(\text{CH}_3)_3\text{C}-\text{CF}_2\text{H}$	0.99	(d) 1							t:d = 3:2
$\text{C}_5\text{H}_9\text{F}_3$	NQ	$(\text{CFH}_2)_3\text{C}-\text{CH}_3$	1.05	(g) 1.7	4.4	(d) 47.1					
$\text{C}_5\text{H}_9\text{F}_3$	NK ^{f)}	$(\text{CH}_3)_2\text{C}_2(\text{CFH}_2)_2 (\text{CF}_2\text{H})$	1.06	(m) < 1	4.25	(d) 47.1	5.67	(t) 56.6			m:d:t ~ 7:2:1
$\text{C}_5\text{H}_8\text{F}_4$	NS	$\text{C}(\text{CH}_2\text{F})_4$									
$\text{C}_5\text{H}_8\text{F}_4$	NN	$(\text{CH}_3)_2\text{C}(\text{CF}_2\text{H})_2$	1.3								s:t ~ 3:1
$\text{C}_5\text{H}_8\text{F}_4$	NO	$(\text{CFH}_2)_2\text{C}(\text{CF}_2\text{H})(\text{CH}_3)$	1.1								s:m:t ~ 3:4:1
$\text{C}_5\text{H}_7\text{F}_5$	NT	$(\text{CFH}_2)_3\text{C}-\text{CF}_2\text{H}$				4.66	(d) 46.6	6.0	(t) 54.7		
$\text{C}_5\text{H}_6\text{F}_6$	NR	$(\text{CFH}_2)_2\text{C}(\text{CF}_2\text{H})_2$				4.7	(d) 46.4	6.1	(t) 54.4	d:t ~ 6:1	d:t = 2:1
$\text{C}_5\text{H}_5\text{F}_7$	NP	$(\text{CF}_2\text{H})_3\text{C}-\text{CFH}_2$				4.9	(d) 46.1	6.2	(t) 54.2		
$\text{C}_5\text{H}_4\text{F}_8$	NK	$\text{C}(\text{CF}_2\text{H})_4$									
$\text{C}_5\text{H}_4\text{F}_8$	NI	$(\text{CF}_2\text{H})_2\text{C}(\text{CF}_3)(\text{CFH}_2)$				4.95	(d) 46	6.24	(t) 54		
$\text{C}_5\text{H}_3\text{F}_9$	NH	$(\text{CF}_2\text{H})_3\text{C}-\text{CF}_3$									
$\text{C}_5\text{H}_3\text{F}_9$	NG	$(\text{CF}_3)_2\text{C}(\text{CFH}_2)(\text{CF}_2\text{H})$				4.92	(d) 45.6	6.31	(t) 52.2	f)	
$\text{C}_5\text{H}_2\text{F}_{10}$	NE	$(\text{CF}_3)_2\text{C}(\text{CF}_2\text{H})_2$									
$\text{C}_5\text{H}_1\text{F}_{11}$	NC	$(\text{CF}_3)_3\text{C}-\text{CF}_2\text{H}$									
C_5F_{12}	NB	$\text{C}(\text{CF}_3)_4$									

a) Chemical shifts δ [in ppm] are relative to TMS; they were calculated by assuming that the residual proton on CDCl_3 occurs at 7.26 on δ -scale.

b) d = doublet, t = triplet, q = quadruplet, m = multiplet (Note: only basic splittings are given)

c) This signal is a very weak triplet, which does not appear in the print out.

d) from: F. A. Bovey, "Nuclear magnetic resonance spectroscopy," 1969.

e) complex multiplet between 4.3 and 4.6 ppm.

f) data from LTG products.

Mass spectral data for the partially fluorinated neopentanes are not conclusive, because (except for mono-fluoro- and difluoroneopentane) no molecular ion or molecular ion minus fluorine was found. Mass spectral data for the compounds are listed together with their IR spectra in Table 17. Two minor fractions (NM and NF) have not yet been identified, because (from NMR spectra) they obviously consist of mixtures of two or more different compounds. Compounds NS and NT have almost the same retention times on column QF-1. For this reason both of them contain a substantial amount (~20%) of each other. In this case both could be clearly identified from their NMR spectra (by comparison of relative integrations). Only IR and mass spectra can not be listed, because it is not clear, which bands (or masses, respectively) belong to which compound.

TABLE 17

IR AND MASS SPECTRA FOR PARTIALLY FLUORINATED NEOPENTANES:

NF = 1-fluoroneopentane C₅H₁₁F

IR: 2960 (vs), 2890 (ms), 1480 (m,br), 1410 (w), 1400 (w), 1380 (sh), 1370 (m), 1360 (sh), 1290 (w,br), 1220 (w,br), 1190 (w), 1045 (s), 1025 (m), 1015 (s), 1005 (m), 905 (w)

MS: CI: 89 (1.1) C₅FH₁₀ (M-H); 75 (2.8) C₄FH₈ (M-CH₃); 71 (100) C₅H₁₁ (M-F); 69 (3.0) C₅H₉; 59 (1.0) C₃FH₄

EI: 75 (38.5) C₄FH₈; 57 (100) C₃FH₂ or C₄H₉; 55 (61.1) C₃F or C₄H₇; 47 (57.1) C₂FH₄; 41 (81.6) C₃H₅; 39 (47.3) C₃H₃; 33 (25.8) CFH₂; 29 (71.2) C₂H₅; 27 (37.1) C₂H₃.

NL = 1,3-difluoroneopentane C₅H₁₀F₂

IR: 2970 (s), 2900 (m), 1480 (m), 1405 (w), 1370 (w); 1055, 1050, 1040, 1030 (vs); 995, 990 (mw), 910 (w)

MS: CI: 89 (38.3) C₄F₂H₃; 75 (18.1) C₃F₂H; 69 (100) C₄FH₂ or C₅H₉; 59 (45.6) C₃FH₄

EI: 75 (89.7) C₃F₂H; 73 (10.4) C₄FH₆; 69 (17.7) C₄FH₂ or C₅H₉; 59 (16.0) C₃FH₄; 55 (76.1) C₄H₇ or C₃F; 53 (12.2) C₄H₅; 51 (12.1) CF₂H or C₄H₃; 47 (100) C₂FH₄; 41 (23.5) C₃H₅; 39 (36.3) C₃H₃; 33 (48.8) CFH₂; 29 (58.1) C₂H₅; 27 (44) C₂H₃.

NF' = 1,1-difluoroneopentane C₅H₁₀F₂

IR: 2970 (m), 2880 (w), 1490 (w,br), 1410 (w), 1370 (w), 1290 (w,br), 1110 (s), 1100 (ms), 1085 (ms), 1080 (s), 1030 (mw), 905 (w)

MS: CI: 89 (100) C₅H₁₀F (M-F); 87 (1.8) C₅H₈F; 71 (4.2) C₅H₁₁; 69 (11.5) C₄FH₂ or C₅H₉; 59 (5.1) C₃FH₄

EI: 65 (44.6) C₂F₂H₃ or C₅H₅; 57 (100) C₃FH₂ or C₄H₉; 51 (30.5) CF₂H or C₄H₃; 47 (18.4) C₂FH₄; 41 (88.3) C₃H₅; 39 (35.1) C₃H₃; 29 (45.4) C₂H₅; 27 (22.2) C₂H₃

TABLE 17 (CONTINUED)

NO = Sym. trifluoroneopentane C₅H₈F₃

IR: 2970 (m), 2900 (mw), 1470 (w,br), 1390 (w,br), 1290 (w,br),
 1200 (w,br), 1050/1040 (vs), 980 (w), 935 (vw)
 MS: CI: 117 (40.6) C₅F₃; 87 (100) C₄F₂H or C₅H₆F; 67 (29.9) C₄F or
 C₅H₇; 59 (64.3) C₃FH₄
 EI: 77 (11.6) C₃F₂H₃; 59 (20.7) C₃FH₄; 53 (20.4) C₄H₅; 51 (19.3)
 C₄H₃; 47 (100) C₂FH₄; 43 (12.1) C₂F; 41 (15.1) C₃H₅; 39 (23.5)
 C₃H₃; 33 (47.8) CFH₂; 29 (19.4) C₂H₅; 27 (26.8) C₂H₃.

NK' = asym. trifluoroneopentane C₅H₈F₃

IR: 2980 (ms); 2900 (w), 1480 (w), 1410 (w), 1370 (w), 1190 (v),
 1120 (s), 1110 (ms), 1100 (sh), 1090 (s), 1040 (sh), 1030 (s),
 990 (w), 905 (w)
 MS: CI: 117 (100) C₅F₃; 87 (66.5) C₄F₂H; 67 (17.5) C₄F
 EI: 93 (14.3) C₃F₃; 75 (100) C₃F₂H; 65 (68.5) C₅H₅; 59 (14.5)
 C₃FH₄; 55 (61.8) C₃F; 51 (30.3) CF₂H; 47 (71.0) C₂FH₄;
 43 (10.9) C₂F; 41 (11.4) C₃H₅; 39 (20.1) C₃H₃

NN = 1,1,3,3-tetrafluoroneopentane C₅H₆F₄

IR: 2980 (w,br), 1470 (w,br), 1390 (mw,br), 1240 (mw), 1215 (m),
 1180 (m), 1145 (sh), 1130 (ms), 1100 (s), 1080 (sh), 980 (w),
 660 (w)
 MS: CI: 141 (100) C₅F₄H₃
 EI: 69 (14.8) C₄FH₂ or C₅H₉; 65 (10.5) C₅H₅; 64 (14.0) C₅H₄;
 59 (55.3) C₃FH₄; 57 (12.2) C₃FH₂; 51 (100) CF₂H 39 (15.2) C₃H₃

NO = asym. tetrafluoroneopentane C₅H₆F₄

IR: 2980 (m), 2900 (w), 1470 (w,br), 1410/1390/1370 (w,br),
 1280 (w), 1210, 1190 (br), 1090 (s,br), 1030 (s), 975 (w),
 930 (w) 900 (vw), 840 (vw), 690 (w), 640 (vw)

TABLE 17 (CONTINUED)

MS: CI: 133 (14.8) $C_3F_5H_2$?; 125 (14.7) C_4F_4H ; 119 (18.9) $C_5F_3H_2$
117 (100) C_5F_3 ; 105 (56.1) C_4F_3 ; 85 (46.0) C_5FH_6 ; 75 (52.6)
 C_3F_2H ; 73 (12.8) C_4FH_6
EI: 93 (26.5) C_3F_3 ; 77 (15.7) $C_3F_2H_3$; 73 (48.6) C_4FH_6 ; 71 (10.7)
 C_4FH_4 ; 59 (27.2) C_3FH_4 ; 53 (16.9) C_4H_5 ; 59 (27.2) C_3FH_4 ;
53 (16.9) C_4H_5 ; 51 (61.2) CF_2H 47 (100) C_2FH_4 ; 41 (23.4) C_3H_5 ;
39 (28.1) C_3H_3 ; 33 (35.8) CFH_2 ; 29 (10.7) C_2H_5 ; 27 (17.4)
 C_2H_3

NR = hexafluoroneopentane $C_5H_6F_6$

IR: 2980 (mw), 2910 (w), 1480 (w), 1390 (m), 1290 (w,br), 1190 (s),
1110 (s,br), 1060 (sh), 1040 (sh), 970 (w), 910 (m), 670 (w)
MS: CI: 141 (100) $C_5F_4H_5$; 121 (11.4) $C_5F_3H_4$; 91 (25.0) $C_4F_2H_5$; 77
(49.6) $C_3F_2H_3$; 65 (31.9) C_5H_5 ; 59 (61.0) C_3FH_4
EI: 95 (45.3) $C_3F_3H_2$; 91 (10.1) $C_4F_2H_5$; 89 (12.2) $C_4F_2H_3$; 77
(80.6) $C_3F_2H_3$; 65 (10.0) C_5H_5 ; 59 (100) C_3FH_4 ; 57 (19.2)
 C_3FH_2 ; 51 (75.1) CF_2H ; 39 (12.4) C_3H_3 ; 33 (12.5) CFH_2

NP = heptafluoroneopentane $C_5H_5F_7$

IR: 3000 (sh), 2975 (w), 2900 (sh), 1480 (w), 1390 (m), 1190 (vs,
with several shoulders), 1110 (s), 1070 (s), 1030 (sh), 945
(w), 790 (w), 600 (w)
no MS due to impurities of peak NF.

NK = sym tetrahydryl-F-neopentane $C_5H_4F_8$

IR: 3000 (w), 1395 (m), 1365 (w), 1215 (ms), 1190 (vs), 1145/
1140 (m), 1120 (ms), 1100 (m), 1060 (m), 690 (m)
MS: CI: 107 (48.8) $C_4F_3H_2$; 127 (89.2) $C_4F_4H_3$; 87 (100) C_4F_3H
EI: 75 (18.1) C_3F_2H ; 57 (19.5) C_3FH_2 ; 51 (100) CF_2H ; 47 (15.7)
 C_2FH_4

TABLE 17 (CONTINUED)

NI = asym tetrahydryl-F-neopentane C₅H₄F₂

IR: 3000 (w), 1400 (w), 1380 (m), 1305 (m), 1260 (sh), 1240 (vs),
1170 (m), 1120 (s), 1110 (sh), 1060 (s), 1025 (mw), 680 (mw)

MS: CI: 145 (100) C₄F₅H₂; 125 (11.8) C₄F₄H; 119 (12.1) C₅F₃H₂; 117
(11.1) C₅F₃;

EI: 75 (13.4) C₃F₂H; 69 (17.0) CF₃; 51 (100) CF₂H 33 (16.6) CFH₂

NH = sym tetrahydryl-F-neopentane C₅H₃F₉

IR: 3000 (w), 1380 (m), 1275 (s), 1240 (s), 1170 (m), 1100 (m),
1055 (m), 1010 (mw), 980 (w), 690 (mw), 660 (w)

MS: CI: 127 (100) C₄F₄H₃

EI: 77 (3.6) C₃F₂H₃; 69 (12.1) CF₃; 57 (3.1) C₃FH₂; 51 (100) CF₂H;
31 (4.7) CF

Intensity symbols used in IR-Listings are:

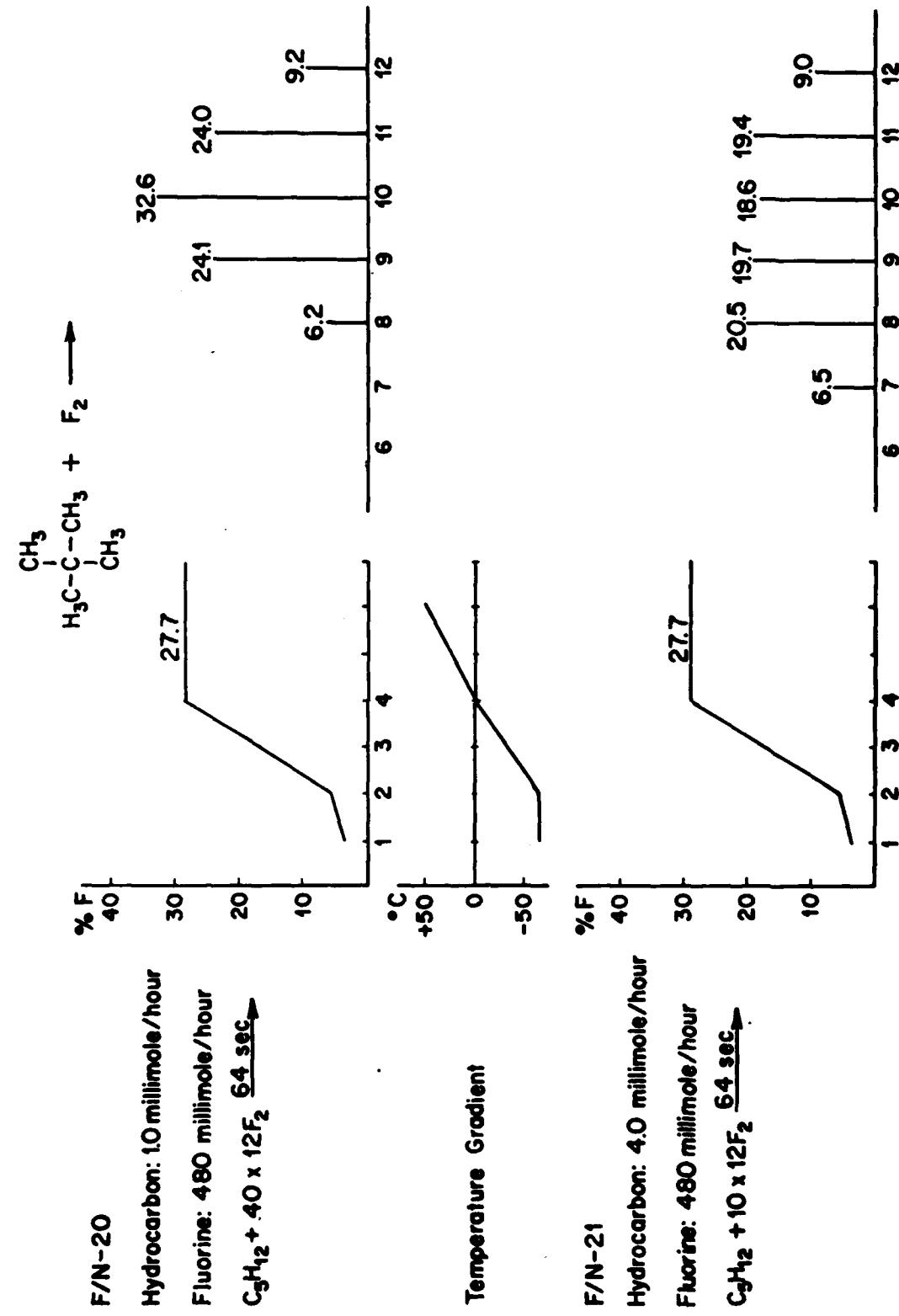
vs very strong, s strong, ms medium-strong, m medium, sh shoulder,
mw medium-weak, w weak, vw very weak, br broad.

Twenty-one independent reactions with neopentane were run and the results compared. In each of these reactions variables such as carrier flow, fluorine concentration gradient, reaction time and hydrocarbon mass throughput were changed. Repetative runs were made, generally only one variable at a time was changed so as to ascertain its effect on product distributions. In none of the reactions outlined in Tables 11-13 was the reactor or reaction uncontrolled or perceptively violent even in those runs involving fluorine flows exceeding 200 cc/minute (480 mmoles/hr). The product distribution for neopentane as a function of the fluorine concentration gradient is given in Figure 7. In this diagram isomers are combined to illustrate the degree of fluorination obtained as a function of fluorine concentration, concentration gradient, relative F_2 :h.c. stoichiometry and reaction time. It is quite evident that a gaussian distribution of products is approached. This is seen most clearly in reactions F/N-1, F/N-11, F/N-17 and F/N-20. Significant deviations however occur for certain sets of conditions. The most readily explicable is that illustrated by F/N-21 (Figure 8). In this reaction only the hydrocarbon throughput was increased (four-fold) relative to F/N-20. This effect, a compression of the maximum toward lower substitution, is undoubtedly due to fluorine concentration gradient changes as the increased hydrocarbon throughput consumes additional fluorine. The molar amount of fluorine is not at every point much greater than the molar amount of hydrocarbon. This effect is reproducible.

The preceding discussion indicates that fluorination occurs stepwise under our conditions and that product distributions with regard to degree of fluorination should be readily explainable on simple statistical and kinetic grounds. The question which remains is whether each degree of fluorination exhibits a distribution of isomers based on simple statistics. In this regard it became necessary to identify each possible isomer, its

FIGURE 8

NEOPENTANE PRODUCT DISTRIBUTION



statistical weight based upon the assumption of stepwise fluorination, and the comparison of the theoretical with the experimental distribution of isomers. Because of the nature of the aerosol process, the assumption that only effects due to statistical weighting or internal directive effects should be important is a defendable one. The basic process involves finely dispersed hydrocarbon particulates in a gaseous helium matrix which are subjected to diffusion controlled attack by gaseous fluorine. Fluorine is injected evenly along the reactor length so as to produce a dynamic fluorine concentration gradient which is ideally at equilibrium. Fluorine concentration should be a constant at any given point along the reactor length. This unique set of conditions approximates the conditions produced by a molecular beam apparatus where two reactants intersect and react in a manner governed by condition dependent statistical probability as operated on by the intrinsic reactivities of the reactants themselves. In the aerosol system the intersecting points are random; diffusion controlled, and compound permitting only a statistical treatment and an approximate one at that. It should however be possible to achieve a qualitatively valid comparison between experiment and theory. The results of this are to be presented in Technical Report No. 3 now in manuscript.

The Aerosol Fluorination of Cyclohexane and 1,4-Dioxane in a Four-stage Reactor.

a) Cyclohexane

Reaction conditions for the aerosol fluorination of cyclohexane in the four-stage reactor D are given in Table 18 (F/C-21). Work-up of the product mixture was described in part one. Analytical GLC showed, that the major part of the material had shorter retention times than products from the single-stage fluorinations of cyclohexane, indicating that the materials are

TABLE 18

REACTION CONDITIONS FOR AEROSOL FLUORINATIONS OF CYCLOHEXANE AND
1,4-DIOXANE IN A FOUR-STAGE REACTOR

Ref. No.	Reactor*	hydrocarbon carrier mmoles/h	F ₂ flows [cc/min] in stage	F ₂ dil. He flows [cc/min]				
				1	2	3	4	Σ
Cyclohexane:								
F/C-21	D	1	14	20	20	60	100	200
F/C-22	E	1	14	20	20	60	100	200
Dioxane:								
F/D-12	E	1	63.5	20	20	60	100	200

continued below

Ref. No.	hc:F ₂	reaction time				[min]		
		1	2	3	4			
F/C-21	1:480	4	4	12	20	40	31.5	1.2
F/C-22	1:480	4	4	12	20	40	31.5	2.4
F/C-12	1:480	6	6	18	30	60	29.2	2.2

*temperatures:

Reactor	Module 1	Module 2	coil 1	coil 2
D	-65°C	-30°C	0°C	45°C
E	-65°C	-30°C	0	RT

main carrier was 400 cc/min in all runs.

more highly fluorinated. This is confirmed by the IR-spectra, which show much stronger CF-bands and weak CH-bands. Mass spectra of two of the compounds could be interpreted as from a tetrahydryl-octafluoro- and a trihydryl-nonafluoro cyclohexane, MS of the other compounds do not give as high masses. Only a trace of perfluorocyclohexane was isolated in the two reactions performed to date.

Increasing the reaction time by adding a second copper coil (15 m long) in the second reaction (F/C-22) did not change the composition of the product mixture significantly.

b) 1,4 Dioxane

Reaction conditions for the aerosol fluorination of 1,4-dioxane are also given in Table 18. Work up was the same as in the earlier dioxane fluorinations. The product distribution for this reaction (estimated from areas of GC-peaks) is given in Table 19. This is shown graphically in Figure 9.

Perfluoro-1,4-dioxane was identified by IR (comparison with spectrum of an authentic sample). 2H-F-1,4-dioxane was identified by IR and mass spec: CI: 81 C₂F₃ (100); 195 M-19 (97.3); 99 C₂OF₃H₂ (23.8); 51 CF₂H (11.8). All other compounds were the same as those obtained in previous dioxane fluorinations.

Results and Discussion

Summary

The multistaged aerosol fluorination reactor achieves optimum control over the potentially violent direct fluorination reaction. This system meets all of the criteria enumerated earlier which we, by experience, believe contribute to high yield direct fluorination reactions. It additionally has other distinct advantages in that the degree of fluorination may be

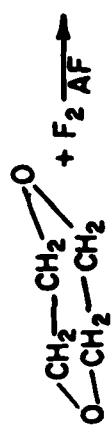
TABLE 19

PRODUCT DISTRIBUTION FROM THE AEROSOL FLUORINATION OF 1,4-DIOXANE IN THE FOUR-STAGE REACTOR E (F/D-12) (ESTIMATED FROM AREAS OF GLC-TRACES)

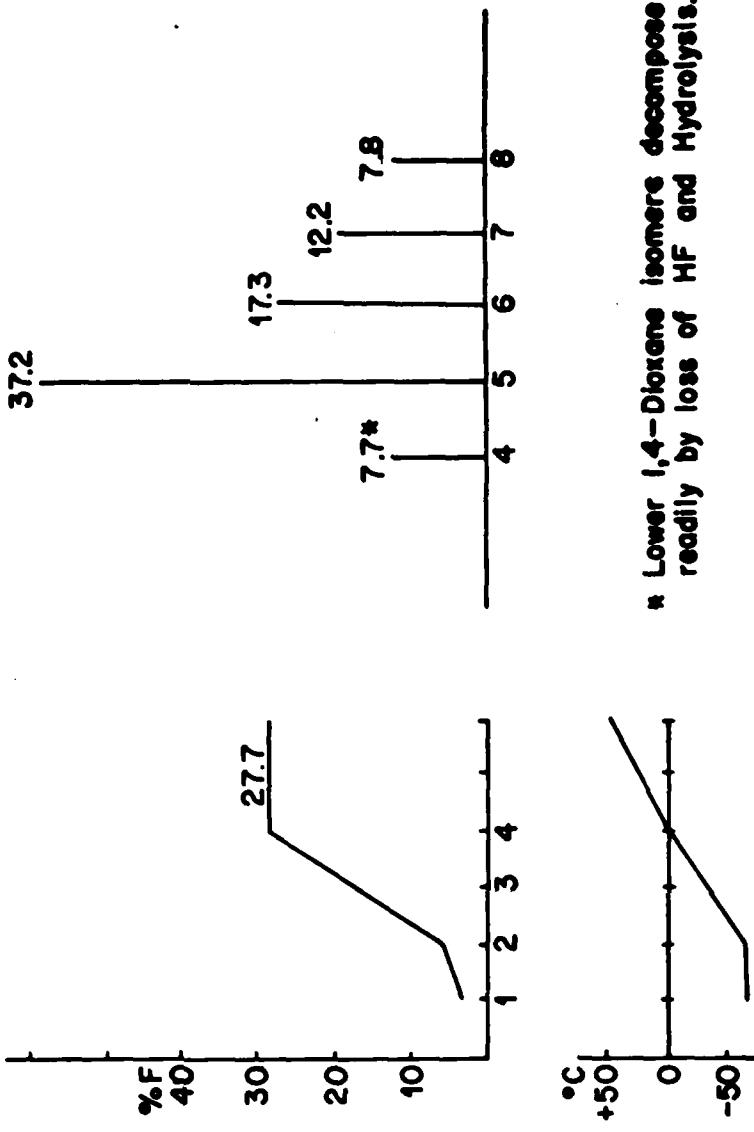
Code	product	%
	perfluoro-1,4-dioxane	7.8
DA (A_4)	2-hydryl- <u>F</u> -1,4-dioxane	12.2
DN (E_3')	dihydryl- <u>F</u> -1,4-dioxane	17.3
DO (E_3'')	trihydryl- <u>F</u> -1,4-dioxane	8.6
DI + DK	trihydryl- <u>F</u> -1,4-dioxane	5.7
DL (E_2')	trihydryl- <u>F</u> -1,4-dioxane	6.4
DM (E_2'')	trihydryl- <u>F</u> -1,4-dioxane	16.5
DG (E')	tetrahydryl- <u>F</u> -1,4-dioxane	4.9
DH (E'')	tetrahydryl- <u>F</u> -1,4-dioxane	2.8

FIGURE 9

1,4-DIOXANE PRODUCT DISTRIBUTION



F/D - 42
 Hydrocarbon: 1.0 millimole/hour
 Fluorine: 4.80 millimole/hour
 $\text{C}_4\text{H}_8\text{O}_2 + 60 \times 8 \text{ F}_2 \xrightarrow{2.2 \text{ min}}$



* Lower 1,4-Dioxane isomers decompose readily by loss of HF and Hydrolysis.

Temperature Gradient

controlled; it is a flow process; the process does not depend on the physical properties of the reactant to be fluorinated; reactant throughputs may be varied over a considerable range for a given design; fluorine concentration and temperature conditions may be tailored to the reactivity of the reactant; and most importantly the observation of nonstatistical substitution effects to be outlined in Technical Report No. 3, suggests that this system might permit the elusive achievement of selectivity in direct fluorinations.

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